Final Report No. IITRI-M08020-82
Contract No. NAS8-31906

SPACE STABLE THERMAL CONTROL COATINGS

George C. Marshall Space Flight Center
Marshall Space Flight Center, AL 35812

Prepared by:

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November 1982

Final Report for Period
1 March 1976 — 30 April 1982

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FOREWORD

This Final Report No. IITRI-M06020-62 under Contract No. NAS8-31906, "Space Stable Thermal Control Coatings," summarizes work initiated in March 1976 and concluded in April 1982. The bulk of the work was performed by March of 1978; subsequent work consisted of limited laboratory studies and space simulation tests. The studies have resulted in a spacecraft thermal control coating designated YB-71, a silicate-bonded zinc orthotitanate system.

Personnel of IITRI who have contributed to this program incluues: W. R. Logan, H. H. Nakamura, D. Fedor, and W. L. Stepp, pigment preparation and evaluation; and F. O. Rogers, J. E. Brzuskiewicz, and J. E. Gilligan, paint studies and space simulation testing. The work of Ms. Alice Dorries of Marshall Space Flight Center in scanning electron microscopy studies, anc the valuable advice and guidance of D. R. Wilkes, Contracting Officer's Representative, are gratefully acknowledged.

Respectfully submitted,

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Y. Harada
Senior Research Engineer

Approved:
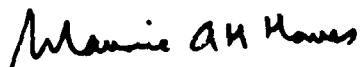
Maurice A. H. Howes, Director
Materials Technology Division

YH:cms

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1. INTRODUCTION

The temperature control of satellites and spacecraft is one of the most challenging technical problems confronting spacecraft designers and materials engineers. The ultimate objective of thermal design is to ensure that the spacecraft operates within a prescribed temperature range defined by the temperature limitations of the vehicle's materials and components.

One of the primary passive methods used to achieve thermal control has been the use of coatings with high reflectance or low solar absorptance (α_s) that are resistant to discoloration in a vacuum-ultraviolet environment. An inorganic pigment that has been found to exhibit high reflectance and stability is ZnO.[1] Two coatings that have been used extensively on various spacecraft are Z-93 and S13G/LO. Both incorporate ZnO as a pigment the former using potassium silicate as a binder and the latter using a methyl silicone.[1] ZnO however. is a strong absorber in the ultraviolet region limiting its ability to reflect solar energy. Therefore, more recent work[2] has been involved with the development of another pigment. zinc orthotitanate (Zn_2TiO_4), which exhibits higher reflectance than ZnO in the near ultraviolet, as shown in Figure 1.

Synthesis of zinc orthotitanate pigment by various ceramic processing methods has been studied on a previous program.[3] Paint formulation and application studies, as well as evaluation and characterization of the physical and optical properties of the paint, have shown this system to exhibit high potential as a new generation thermal control coating. The "MOX" method, i.e., the use of separately precipitated zinc and titanium oxalate precursors, has the distinct advantages of simple and rapid processing and controlled pigment particle size. Thus. this particular synthesis method was emphasized in the current program.

The objective of the current program was to develop a specification quality zinc orthotitanate coating. This report presents the results of various studies conducted on this program which have led to a paint system designated YB-71. This silicate-bonded Zn_2TiO_4 coating is discussed in detail

in the next section. Subsequent sections of this report are devoted to discussions of the different studies which were as follows:

- <u>Pigment Studies</u> - The effects of precursor chemistry, precursor mixing procedures, stoichiometry variations, and of different heat treatments on the physical and optical properties of Zn_2TiO_4.

- <u>Binder Studies</u> - Comparison of inorganic silicate to organic silicone binder systems.

- <u>Paint Studies</u> - The effects of pigment-to-binder ratio, water content, and of different curing procedures on the optical and physical properties of Zn_2TiO_4-potassium silicate coatings.

- <u>Space Simulation Studies</u> - Environmental tests to determine the UV-vacuum stability of coatings for durations up to 5000 equivalent sun hours.
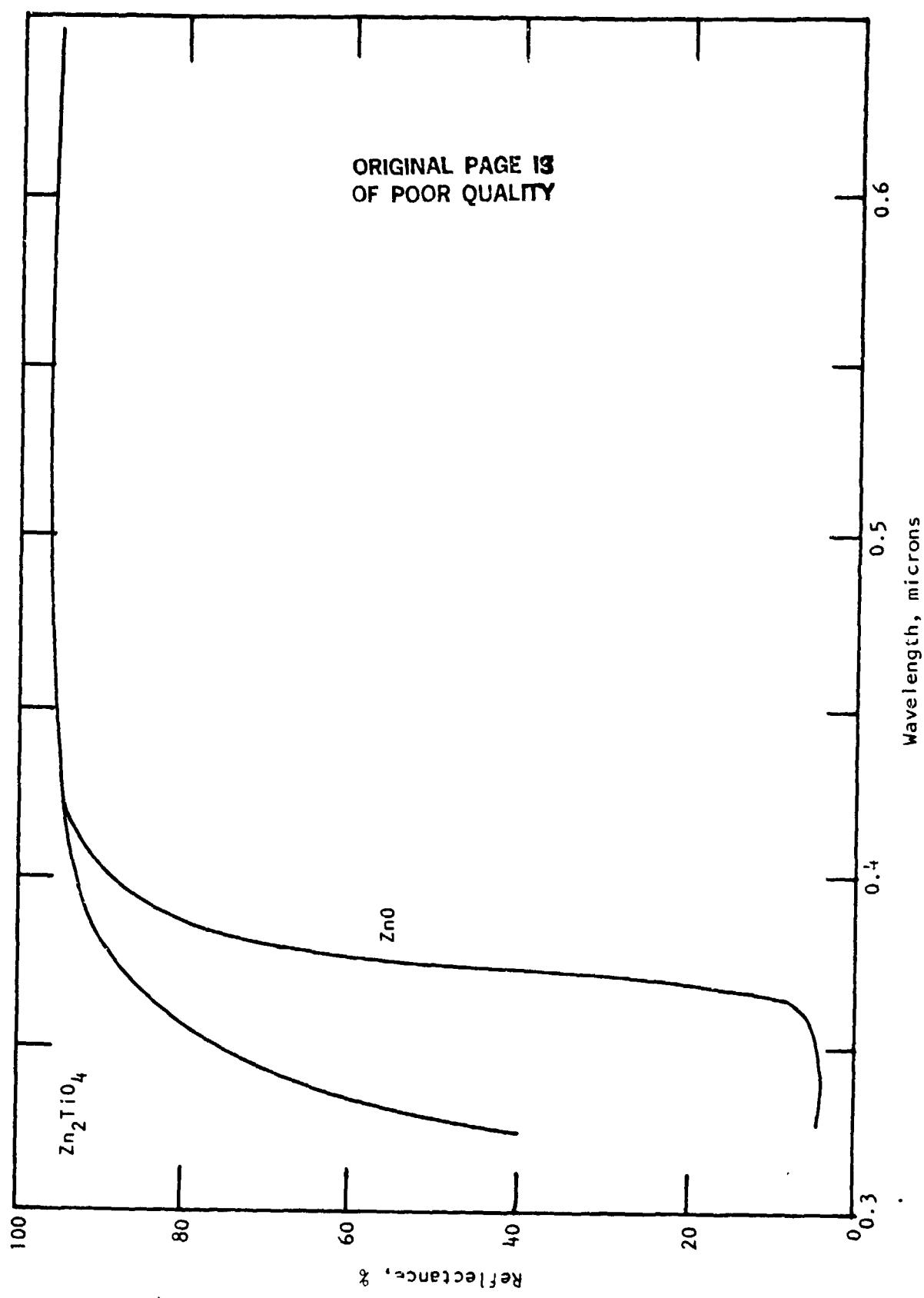
Figure 1. Reflectance spectra of ZnO and Zn_2TiO_4.

2. PAINT SPECIFICATIONS FOR YB-71

2.1 MATERIALS

Zinc orthotitanate pigment is synthesized by an IITRI process termed "MOX " in which zinc and titanium oxalate precursors are fabricated mixed to the correct stoichiometry, pre-reacted at 600°C, and finally flash calcined at 900°C. The binder PS7 potassium silicate, is obtained from Sylvania Electric Products.

2.2 FORMULATION

The materials are mixed in a pigment-to-binder weight ratio (PBR) of 7.1. A typical batch is 100 grams Zn_2TiO_4 30 cc PS7 and an amount of distilled water to give optimum spray viscosity as determined by trial mix. Ball milling is conducted with porcelain balls in a dense alumina mill. A milling time of 2 to 4 hr yields a satisfactory consistency and is recommended.

The paint is formulated just prior to anticipated pplication. Shelf time should be limited to 6 hr, and the mixture should be shaken frequently to resuspend the pigment.

2.3 SUBSTRATE PREPARATION

Substrates should be abraded, e.g., with No. 60 Aloxide metal cloth, using a detergent mixture such as 50% Alconox-50% Comet cleanser. Vigorous scrubbing with as much pressure as the part can tolerate is used. The surface is thoroughly rinsed, checked for water break-free condition and dried. The part is ready for painting, which should be done as soon as possible to assure cleanliness of the substrate.

2.4 APPLICATION

The formulation is applied by spray-painting. The gas pressure should be clean; prepurified nitrogen is a good source. The application technique consists of spraying at a distance of 6 to 12 in. until a reflection due to the liquid is apparent. This is followed by air-drying until the glossy wet

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appearance is practically gone at which time the spraying-drying cycle is repeated. A thickness of about 2 to 3 mils is achieved per cycle. Coating dimensions can therefore be predictably applied. However, hand-spraying is inherently an art. and experience must be gained by the individual painter to determine the most satisfactory technique for him, and his optimum application rate

2.5 CURING

Satisfactory physical properties are obtained by an air cure in a clean environment for not less than 14 days. A temperature of 75° ± 10°F and a relative humidity of 50 ± 25% are recommended.

2.6 REAPPLICATION

The porous nature of a cured coating necessitates heavy spraying when a second coat is applied which yields the characteristic gloss of a satisfactory, finished texture. Wetting of the surface with distilled water spray just prior to painting is also suggested. A fourteen-day lapse should occur after the initial application, prior to reapplication, to assure proper cure of the first coat.

2.7 REPAIR

An area which has been contaminated or damaged should not be cleaned chemically. The defective area should be physically removed by abrading with a ceram c tool which will not leave a residue. The adjoining coated areas should be feather-edged and the area cleaned with surgical gauze wiping and blowing (clean, dry nitrogen). The area can then be repainted using the reapplication technique described above.

2.8 PHYSICAL PROPERTIES

The coating is porous and relatively soft, so that it can withstand stresses well. Samples of YB-71 on aluminum have been subjected to thermal cycling from +225°F to -250°F in a vacuum of 10^{-7} Torr. N deterioration in adhesion was observed as a result of this treatment. Samples have also been cooled to the range of -300°F to -400°F for a period of 45 minutes with no apparent loss in bond integrity.

Soiling tendencies are high, however, due to the porous nature of the coating. Protection from contamination can be provided by a Mylar or Tedlar film which can be placed on the coating after a 10-day cure.

2.9 OPTICAL PROPERTIES

Minimal solar absorptance of about 0.12 can be achieved at a thickness of abouc 8 mils. An emittance of about 0.90 can be expected for YB-71 with a drop to about 0.84 at -220°F.

2.10 UV-VACUUM STABILITY

An increase in α_s of about 0.02 or less can be expected after 5000 equivalent sun-hours (ESH). Emittance is not affected over this exposure time.

3. PIGMENT STUDIES

A great deal of research has been performed to obtain pigment materials stable to the ultraviolet-vacuum environment. Much of the early screening of inorganic powders was conducted at IITRI and has been documented in several reports.[3-5] From this work, zinc oxide and subsequently zinc orthotitanate (Zn_2TiO_4) were determined to be the most stable pigments. The purpose of the current pigment technology studies was to develop methods for producing zinc orthotitanate (Zn_2TiO_4) thermal control pigments of high reflectivity (low α_s) and stability.

3.1 SYNTHESIS OF ZINC ORTHOTITANATE

Synthesis of Zn_2TiO_4 at elevated temperatures by a solid-solid reaction has been reported by several investigators. Bartram and Slepetys[6] described its preparation from anatase titania and zinc oxide by reaction at 800° to 1000°C for 3 hr. Reaction times of 48 hr at 800°C to obtain Zn_2TiO_4 from a zinc oxide-titanic acid reaction have been reported.[7] A phase diagram (Figure 2) for the $ZnO-TiO_2$ system proposed by Dulin and Rase[7] shows the existence of a 1Zn-to-1Ti compound, $ZnTiO_3$, as well as the orthotitanate. Both investigators showed the presence of secondary phases, such as $ZnTiO_3$ ZnO, and/or TiO_2 in their Zn_2TiO_4 products, indicating the need for accurate stoichiometry control to obtain a pure product.

The use of decomposable salt precursors to enhance reaction or sinterability of oxides has been reported by several investigators.[8-10] An example of this enhancement is that of a high-purity $BaTiO_3$ produced from coprecipitated $BaTiO(C_2O_4)_4 \cdot 4H_2O$.[11]

The present study was thus directed toward processing of the zinc- and titanium-source precursors so that rapid conversion to Zn_2TiO_4 under modest time/temperature requirements could be achieved. At the same time it was necessary to modify ultimate firing conditions to minimize sintering effects that are encouraged by such powder processing prior to firing. The various synthesis processes which have been studied in past programs at IITRI are discussed in the following sections.

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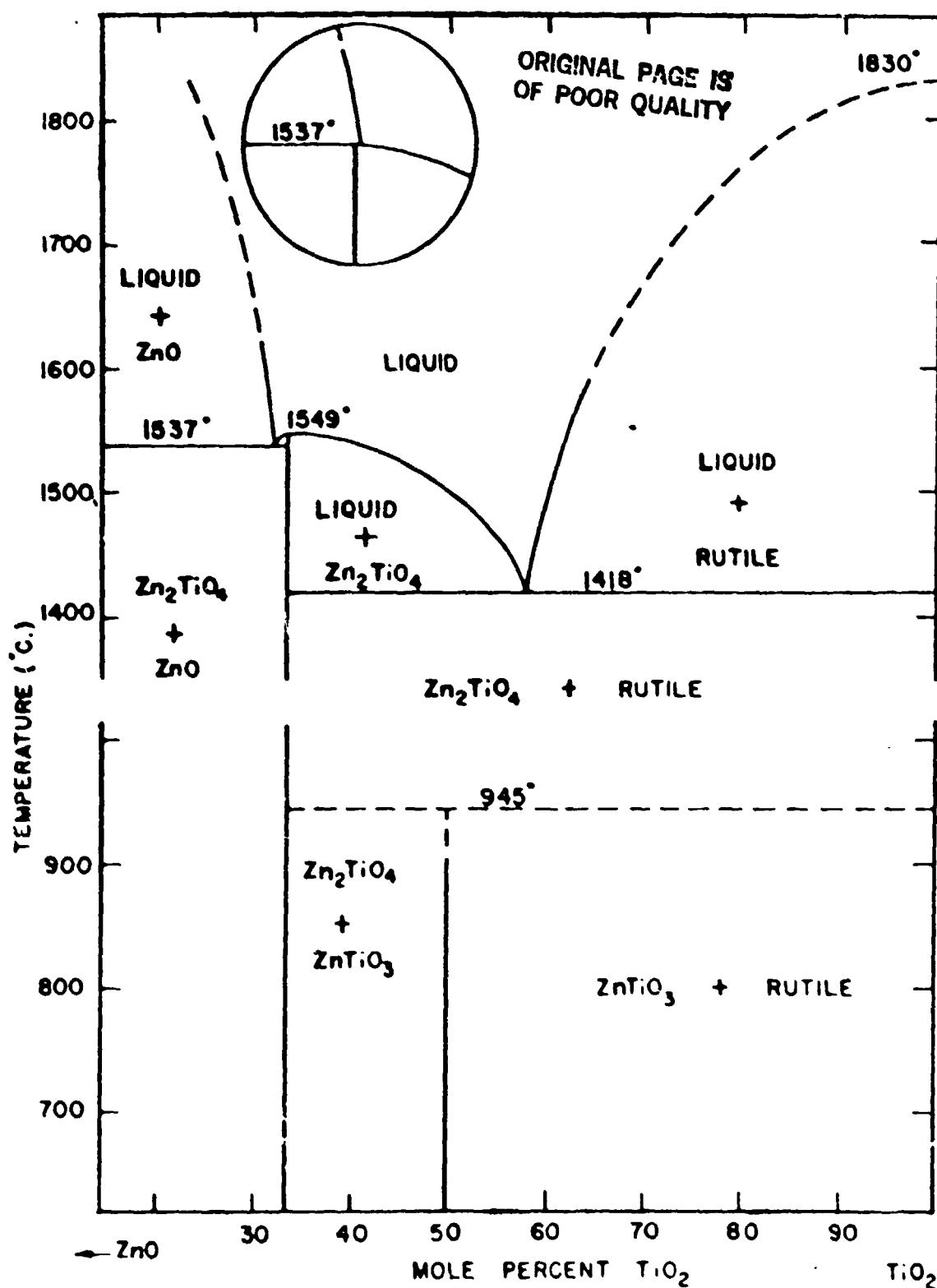
Figure 2.   Phase diagram of the ZnO-TiO$_2$ system.[7]

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3.1.1 Solid State Reaction

The initial method studied at IITRI for producing Zn_2TiO_4 consisted of reacting zinc oxide with titanium dioxide. A series of grinding and mixing operations are carried out at low temperature to assure good particle-to-particle contact and hence, reactivity of the two oxides (Figure 3). Formation of the Zn_2TiO_4 pigment is accomplished by firing at 925°C for 18 hr, additional grinding followed by reactive encapsulation and/or induction plasma calcining[2] to obtain a stable product. A total of 4 hr of wet grinding and 1/2 hr of dry grinding is conducted prior to firing, and this is followed by an additional 12-24 hr of grinding for comminution of the Zn_2TiO_4 product.

The multitude of grinding steps in this process has the disadvantages of long processing times and the dangers of introducing degradable contaminants. Although plasma calcining appear to be favorable for achieving a stable pigment, it involves a rather sophisticated apparatus, and the yield is somewhat low. Another disadvantage of the solid state reaction process is the relatively limited control of the pigment particle size. In view of the limitations, studies of the use of salt precursors for Zn and Ti were conducted in an effort to gain a superior product.

3.1.2 Coprecipitation (COP)

The purpose of the coprecipitation method (COP), shown in Figure 4, is to obtain an intimate mixture of zinc and titanium compounds. This excellent mixing along with the highly reactive nature of the oxides derived upon decomposition of these compounds, permits partial conversion to Zn_2TiO_4 under moderate conditions of 600°C/2 hr. Other investigators[6,7] have shown that higher temperatures and/or longer times are necessary using less reactive zinc and titanium precursors such as the oxides.

The coprecipitation method involves the simultaneous addition of a mixed solution of zinc and titanium chlorides to a solution of oxalic acid. The resulting solution is then heated to, and held at a specified temperature, during which time it is continuously stirred while the precipitate is formed.

Calcination and firings are performed in standard atmospheric electric furnaces. In the 600°C prefiring about 50 wt% of the material is lost as decomposition volatiles. The heating rate to 600°C is maintained at a moderate 1-1/2 hr to accommodate the large evolution of gases during the oxalate decomposition.

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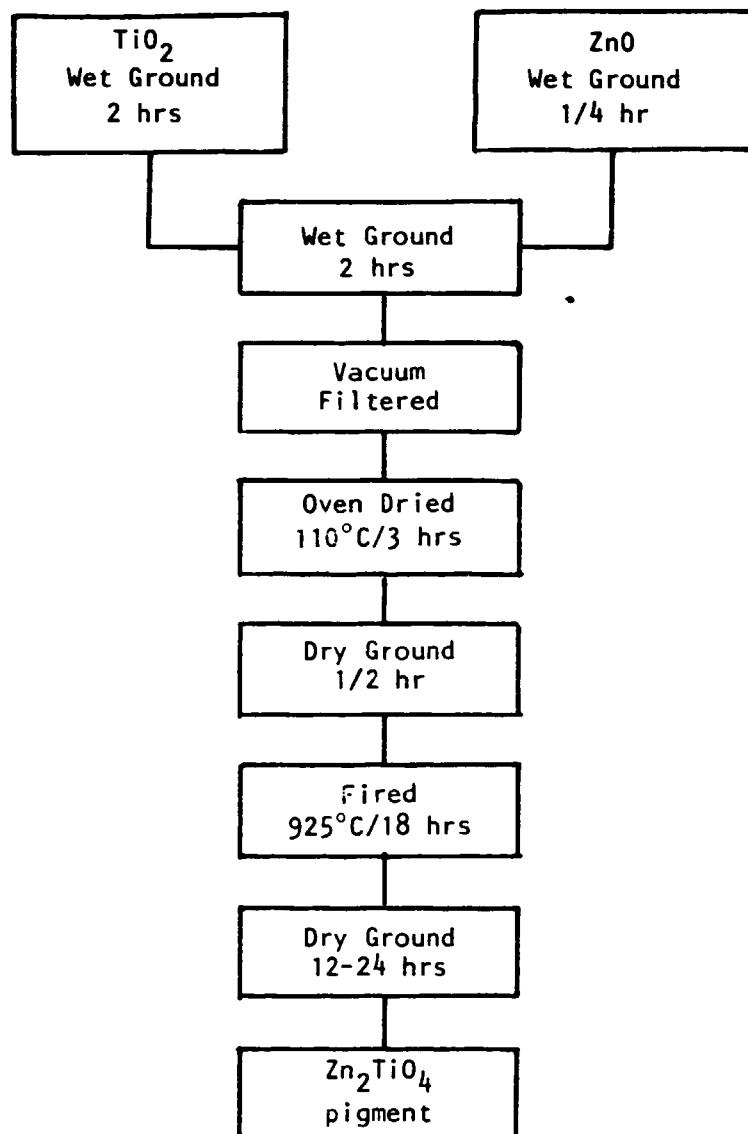
Figure 3. Solid-state process for synthesis of Zn_2TiO_4.

```
┌─────────────┐                  ┌─────────────┐
│   ZnCl₂     │                  │    TiCl₄    │
│  Solution   │                  │   Solution  │
└─────────────┘                  └─────────────┘
```

Figure flow (top to bottom):

- $ZnCl_2$ Solution
- $TiCl_4$ Solution
- Oxalic Acid
- Precipitation 90°C/4 hrs
- Filtration
- Oven Dried 75°C/16 hrs
- Pre-fired 600°C/2 hrs
- Fired 900°C/4 hrs
- Zn_2TiO_4 Pigment
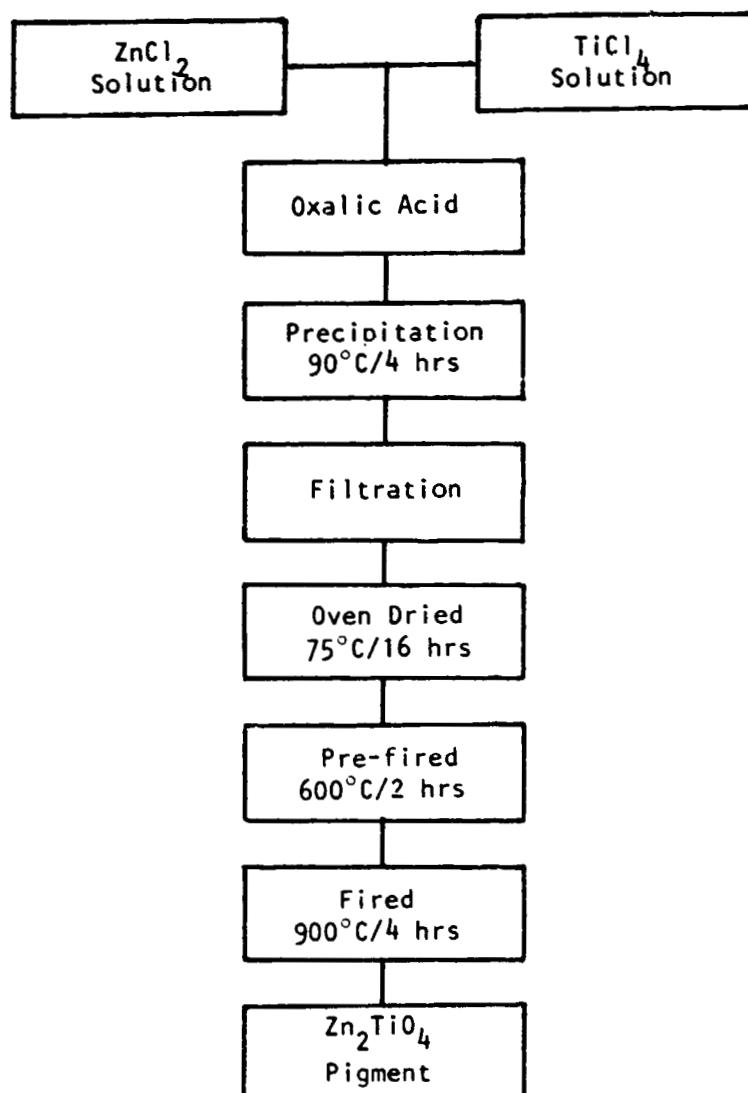
Figure 4.   Precipitation process for synthesis of Zn_2TiO_4.

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Complete conversion to Zn_2TiO_4 was conducted at temperatures from 900° to 1400°C. Firing times of 2 hr were used up to 1300°C; the 1400°C soak time was 5 minutes. To retain the material in unsintered form, samples were fired as loose powders using what may be termed "flash calcination." This involved direct insertion of the powder, which was in a fused silica container, into a furnace at the prescribed firing temperature. Approximately 15 minutes was needed for large batches (1000 g) to attain temperature. Samples were removed in a similar abrupt manner after the prescribed firing time.

A definite advantage of this method is that no grinding is necessary for obtaining pigment particles amenable to incorporation into a paint. Laboratory scale-up studies showed that batches of about 1.5 pounds could be produced; further scale-up may be attainable with larger reaction vessels.

In a previous program,[3] a number of COP materials designated the LH series were evaluated. Optimization of these materials in terms of optical properties and stability was achieved through studies of precipitation parameters, calcination conditions acid leaching for excess ZnO, and encapsulation. The LH pigments can thus be considered a viable backup pigment to the MOX materials which are discussed in the next section.

3.1.3 Mixed Oxalate (MOX) Process

The mixed oxalate studies were conducted to determine if the particle size of the precursor oxalates and the Zn_2TiO_4 obtained from their calcination could be controlled. This investigation was prompted by the observation that COP materials exhibited a tendency toward agglomeration during precipitation. It was believed that this might be avoided through mixing of the separately precipitated and dried zinc and titanium oxalates.

The "MOX" method, distinguished from the COP method, employs two independent and separate steps in the production of the zinc and titanium oxalates. Unlike those in the COP process, the conditions and parameters in the "MOX" method may be separately established and controlled to produce an optimum precipitated product.

Studies[3] have shown that the precipitation conditions for producing an optimum zinc oxalate product differ markedly from those for "TiOX."* In the COP method, the need for a 90°C precipitation condition for "TiOX" requires that the zinc oxalate also be precipitated at this temperature. However it has been shown in our recent studies that zinc oxalate of finer particle size can be obtained at a temperature as low as 10°C. A finer particle size zinc oxalate is desirable from two standpoints: first, to obtain a precursor of fine particle size and, thus, also of the fired product; and second, to obtain improved mixing of zinc oxalate with "TiOX." A closer match of the particle sizes of the zinc oxalate and "TiOX" should improve mixing and enhance the reactivity as well as the uniformity in the reacted binary oxide.

Experimental results showed that a finer particle size zinc orthotitanate could be achieved using the very fine precursors. The MOX process consequently holds a distinct advantage in that conditions for optimum products and yields of zinc oxalate and "TiOX" can be established for each independently. Zn_2TiO_4 obtained by calcination of the mixed "TiOX" and ZnOx precipitates can be utilized as a pigment with no grinding as is the case with the COP process material. A summary of the MOX process currently considered optimum is shown in Table 1.

3.2 "TiOX" CHARACTERIZATION

The reaction of $TiCl_4$ with $H_2C_2O_4 \cdot 2H_2O$ in an aqueous medium of 90°C yields a finely divided white precipitate designated "TiOX." X-ray analysis of this material has revealed a well-defined, reproducible powder pattern from batch to batch. When heated to about 300°C or higher, the material decomposes to TiO_2. The studies discussed in the following sections were conducted in an effort to better characterize the chemical identity of "TiOX."

3.2.1 Gravimetric Analysis

It has been established in previous studies that calcination of "TiOX" at temperatures of 300°C or higher results in the formation of TiO_2 with a weight

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*"TiOX" means precipitate formed by reacting $TiCl_4$ with oxalic acid in an aqueous media at 90°C.

TABLE 1. MIXED OXALATE (MOX) PROCESS FOR SYNTHESIS OF ZINC ORTHOTITANATE

Materials Preparation	Prepare aqueous solutions of $TiCl_4$ (<15°C) and $ZnCl_2$ (room temperature)
Oxalate Preparation	$ZnCl_2$ (aq.) + $H_2(C_2O_4) \cdot 2H_2O$ (aq.) → $ZnC_2O_4 \cdot 2H_2O$ (s) + 2HCl (aq.) (room temperature/1 hr)
	$TiCl_4$ (aq.) + $H_2(C_2O_4) \cdot 2H_2O$ (aq.) → "TiOX" (s) + nHCl (aq.) (90°C/1 hr)
	Each oxalate filtered with copious water washings to pH ≈ 7 and dried at 60°-70°C for >16 hr.
Mixing	Oxalate mixtures to yield 2Zn/1Ti ratio ball milled in nylon bottles with porcelain balls for >10 hr
Pre-calcination	$ZnC_2O_4 \cdot 2H_2O$ + "TiOx" → Zn_2TiO_4 + ZnO + TiO_2 + volatiles (600°C/2 hr, time to 600°C ~ 1 hr)
Flash Calcination	Zn_2TiO_4 + ZnO + TiO_2 → Zn_2TiO_4 (900°C/4 hr) (Reaction goes to completion)
	Insert directly into furnace at 900°C. Time to 900°C about 15-20 minutes Soak for 4 hr. Remove and cool.

loss of about 46%. This weight loss, however, could vary as much as ±1%, thus making the design of exact stoichiometry difficult. The molecular weight assigned to "TiOX" in earlier work was calculated as:

$$\frac{79.90}{x} = 0.54$$

where 79.90 = molecular weight of TiO_2
54.0 = fractional amount of TiO_2 residue
x = molecular weight of "TiOX" = 147 96

If the fractional residues were 0.53 or 0.55, the apparent molecular weight of the "TiOX" precursor would be 150.75 or 145.27 respectively.

During the present studies, the "TiOX" was preconditioned by heating at 80°C for 16 hr folowed by storage in a desiccator over $CaSO_4$. This material was then carefully weighed, converted to TiO_2 at 850°C, and reweighed to determine the fractional residue. The data showed a reproducible value of 143.2 ± 0.1 as the molecular weight of the "TiOX."

These experiments indicate the value of preconditioning in that a more constant (reproducible) precursor of predictable weight loss, and thus TiO_2 product is obtained. This is accomplished through removal of moisture which absorbs on the high surface area "TiOX." Variability in this absorbed water can occur due to temperature and humidity conditions, as well as the amount of activity of the available surfaces of the "TiOX" particles. In contrast, zinc oxalate has been found to be much more stable in storage exhibiting calcination weight losses of 57.02 to 57.10% or very close to the theoretical value of 57.04%. The results of weight loss studies are shown in Figure 5.

Using a Fisher Model 260P differential thermal analyzer programmed for a temperature rise of 10°C per minute, 100 mg samples of "TiOX" and of zinc oxalate were run against 100 mg of fused silica. In the case of "TiOX" the test revealed a single large endotherm starting at approximately 160°C and peaking at 260°C, and no further marked thermal activity to 750°C (Figure 6). The existence of only one relatively sharp endotherm indicates that "TiOX" is not a hydrate; however, water of hydration may be hidden by the large endotherm. The zinc oxalate showed two endothermic peaks typical of hydrate, one beginning at approximately 107°C and peaking at 165°C, followed by a second peak
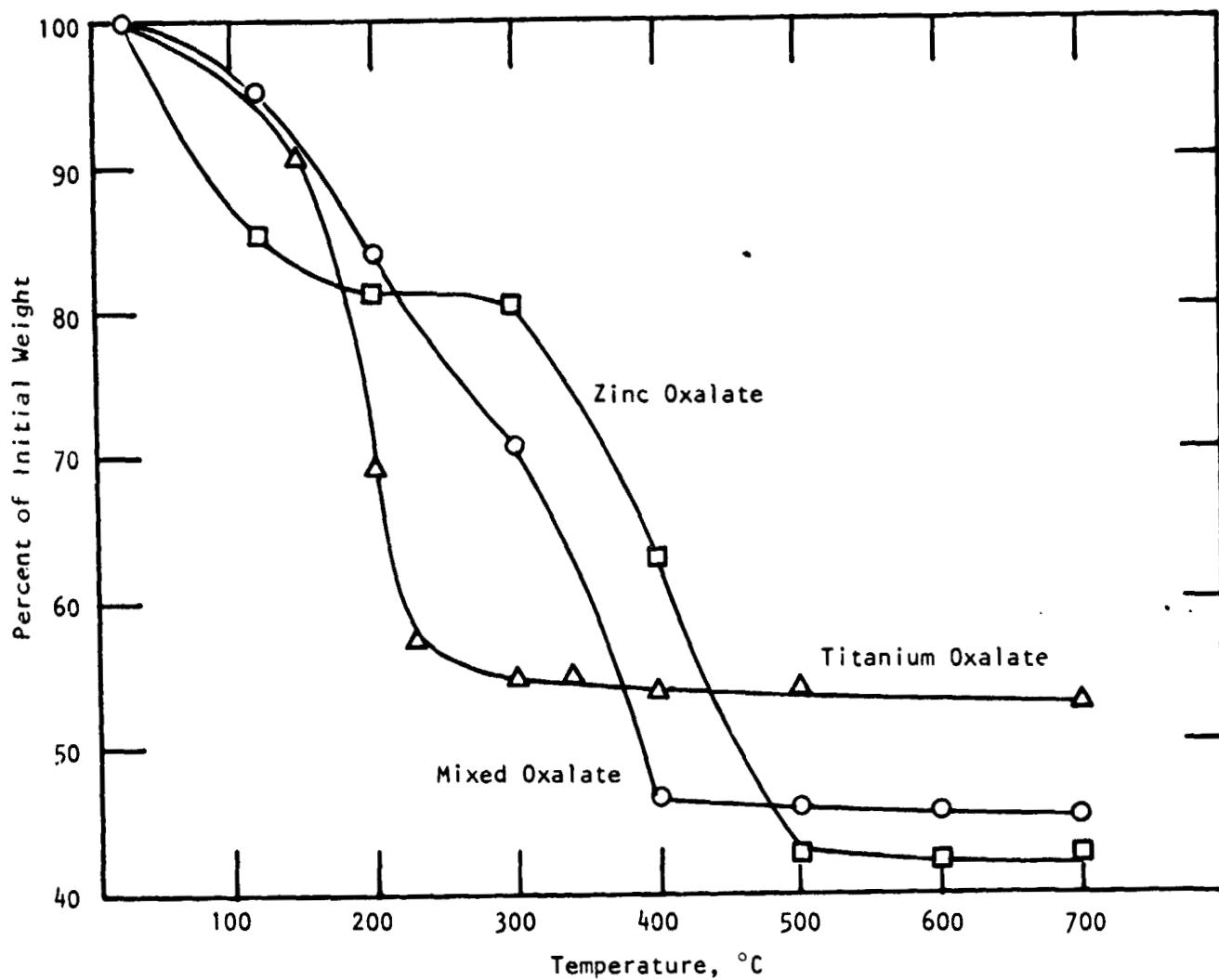
Figure 5. Weight loss vs. temperature for zinc oxalate, titanium oxalate,
and mixed oxalates (2 hrs at temperature).
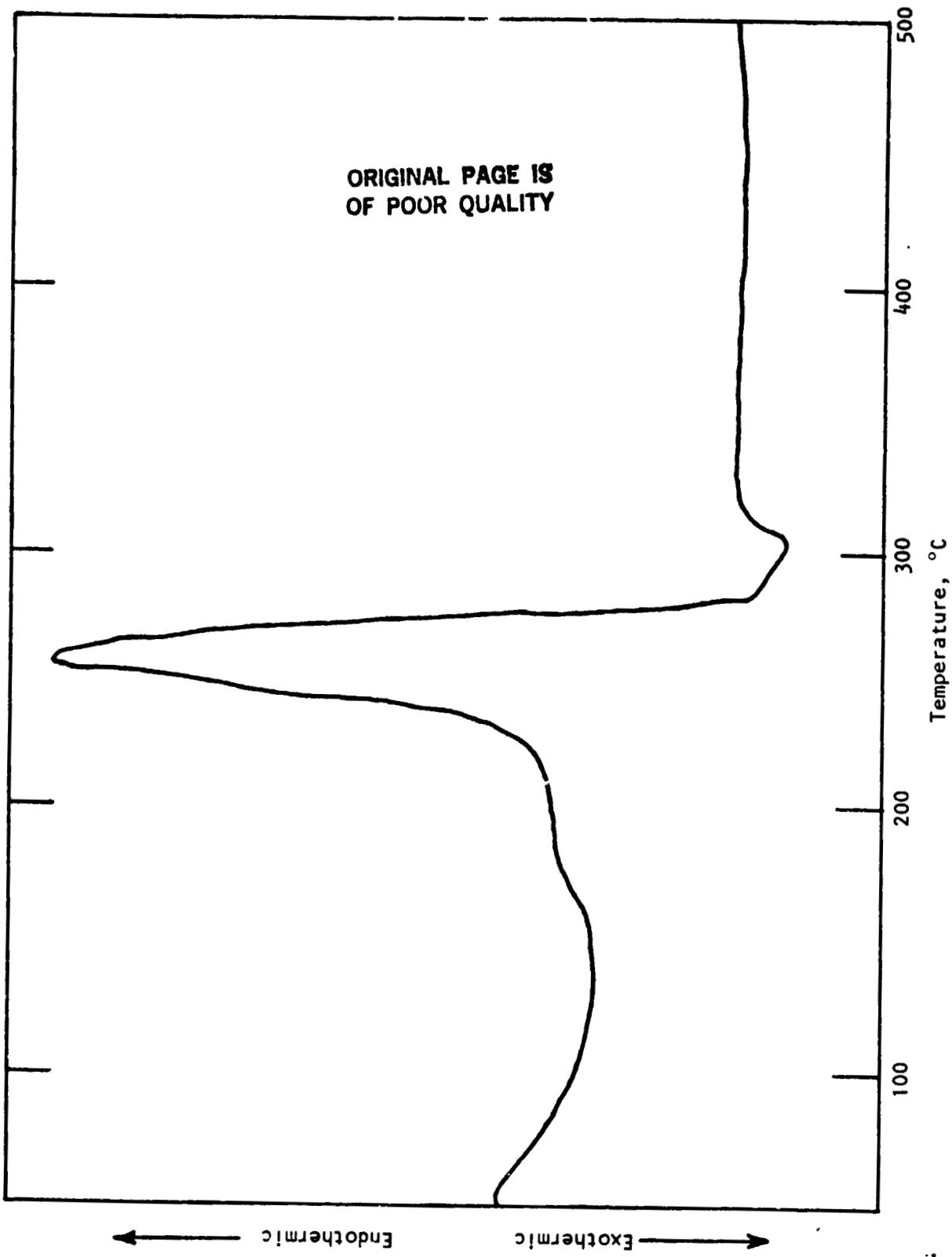
Figure 6. DTA study of "TiOX" decomposition.

beginning slightly above 310°C and peaking at 408°C, and showed no further thermal activity to 750°C (Figure 7).

3.2.2 SEM and X-ray Analysis

Examination of four batches of "TiOX" ("TiOX-2" through "TiOX-5") shows the material to consist of sphere-like aggregates of particles which are less than one micron in size (Figure 8). Good uniformity from batch to batch was evident, and this morphology is similar to that determined on a previous program.

The "TiOX" materials have also been examined using X-ray vsis. Debye-Scherrer powder patterns show that the current materials identical in crystalline structure to that produced in previous programs. This shows that the present preconditioned "TiOX" with a molecular weight of about 143 (as compared to the "old" material of about 147) has had only absorbed surface water removed; loss of chemically combined water would generally result in a change in crystal structure or size.

3.2.3 Chemical Analysis

Characterization of "TiOX" has included chemical analysis, and the results of the analyses of two laboratories are as follows:

Laboratory	Sample	%C	%H
M	1	8.98	1.85
M	2	8.95	1.84
P	3	8.75	2.11
P	4	8.98	2.10

Based on a molecular weight of 143.2, the results from Lab "M" would correspond to 12.85 g of carbon and 2.65 g of hydrogen, which may be translated to one atom of carbon and three atoms of hydrogen. The Lab "P" data would be 12.66 g C and 3.01 g H, or one atom C and three atoms H. Based on these results along with an assumption that the balance is oxygen the atomic makeup of "TiOX" may be written as $Ti(OH)_2CO_3$.
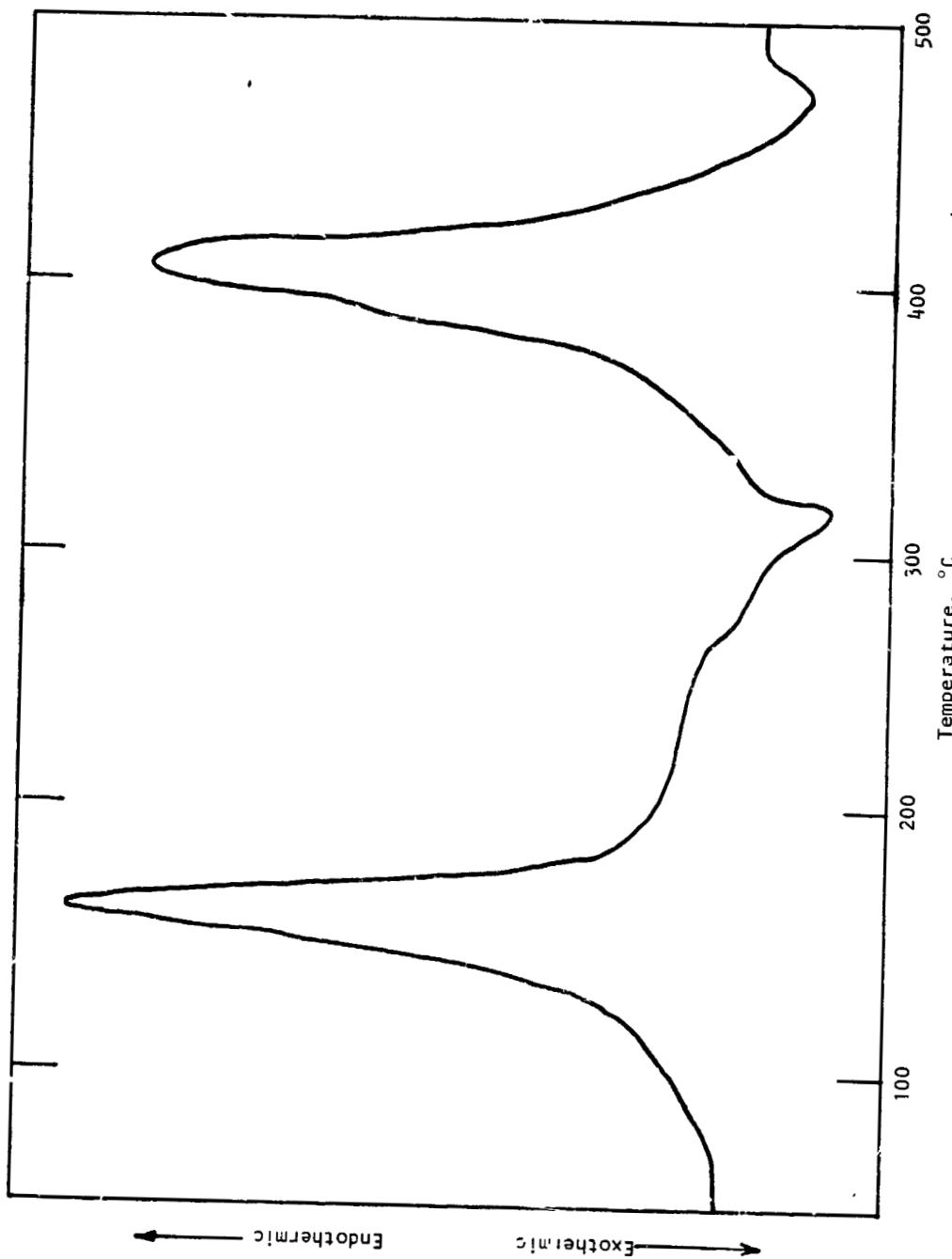
Figure 7. DTA study of zinc oxalate decomposition.

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(a) Batch 2

(b) Batch 3
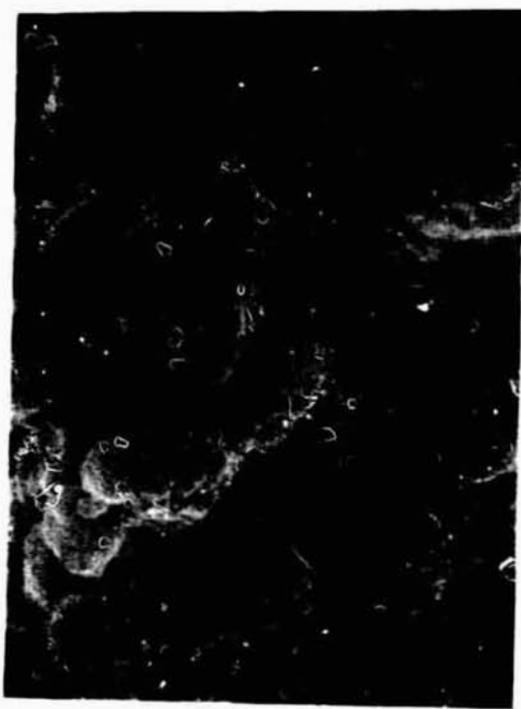
(c) Batch 4

(d) Batch 5
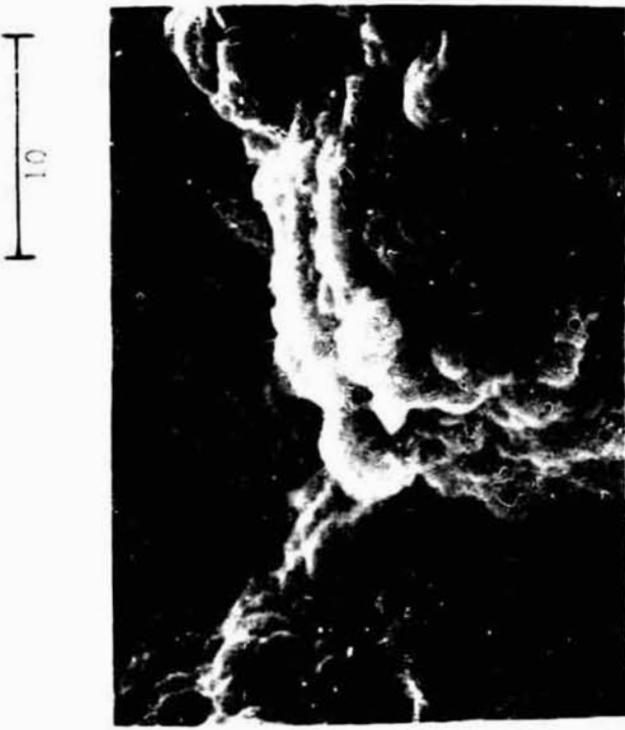
Figure 8. SEM views of "TiOX."

3.2.4 Summary

The "TiOX" characterization studies have shown how it can be rendered into a more reproducible material in terms of weight loss i.e., by the pre-conditioning step. Although the chemical makeup of "TiOX" was not determined precisely, the magnitude of a crystallographic determination was believed to be beyond the scope of this program. The improved reproducibility of "TiOX" was an important outcome in assuring reproducibility of Zn_2TiO_4.

3.3 MIXING STUDIES

Previous methods used to mix "TiOX" with zinc oxalate have involved the use of porcelain balls in glass ball mills. However, this sometimes resulted in the powder mixture sticking both to the balls and the mill wall, leading not only to loss of material, but also to the possibility of a change in the Zn/Ti ratio of the mixture.

Experiments were conducted with polymeric materials, i.e., 1/2 in. nylon balls in polypropylene containers in an effort to preclude such sticking. Mixtures of zinc oxalate with "TiOX" to yield a Zn/Ti ratio of 2 to 1 were ball milled both dry and wet (isopropyl alcohol). After recovery of the materials from the polymeric mills, samples were calcined and evaluated gravimetrically and optically.

The data obtained are summarized in Table 2. General observations are that, after dry mixing, essentially complete recovery of powder was effected; this is reflected in the very small differences in weights before and after mixing. Recovery of powder after wet mixing is somewhat more involved in that the powder must be separated from the liquid (isopropanol) as well as the balls. The added handling necessary resulted in greater weight changes as compared to dry mixing. Mix No. 3 gained 0.75%, and mix No. 4 lost 1.86%.

The samples were subjected to a precalcine of 500°C/2 hr, followed by formation of Zn_2TiO_4 at 900°C/2 hr. The weight losses due to the decomposition-reaction process were all quite close to theoretical as seen in the last column in Table 2.

Reflectance curves of 900°C calcined materials prepared from dry milled and wet milled precursors are shown in Figure 9. Both show a "knee," indicative of excess zinc oxide. The wet milled-based material exhibits the "knee" at lower reflectance, suggesting higher ZnO content.

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TABLE 2. SUMMARY OF MIXING STUDIES

Mix No.	Medium	Material Weight, g		Weight Change, %	Weight % Residue[a]	
		Into Mill	Recovered From Mill		500°C/2 hr	900°C/2 hr
1	Dry	91.75	91.41	-0.37	4..54	45.86
2	Dry	91.75	91.81	+0.06	46.70	46.20
3	Isopropanol	91.75	92.44	+0.75	47.13	46.51
4	Isopropanol	91.75	90.04	-1.86	47.89	47.17

[a]Theoretical: 46.57%
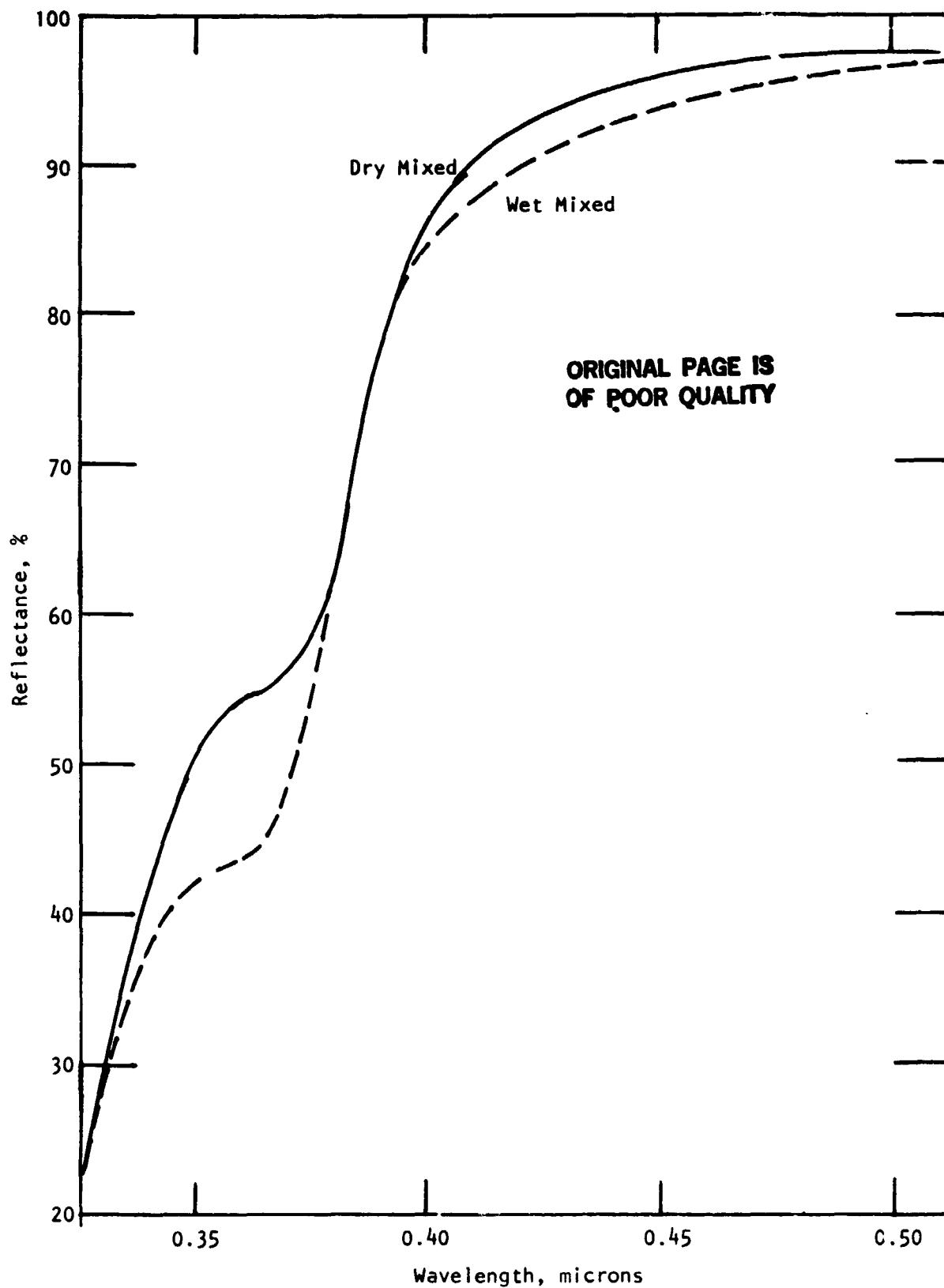
Figure 9. Reflectance spectra of $\bar{}n_2TiO_4$ powders prepared from dry mixed
and wet mixed precursors.

These observations show that the use of polymeric media results in prac-
tically no sticking or loss of powder. This may be due to a "non-charged" na-
ture of the plastics and/or the use of a preconditioned, dried "TiOX." Thus,
this mixing technique minimizes loss of material in milling, and the potential
change in mixture stoichiometry through such loss has been greatly reduced.
This offers a positive step toward definition of engineering specifications
for processing of MOX materials.

3.4 STOICHIOMETRY EFFECTS

In previous studies of stoichiometric effects at IITRI,[3] it has been ob-
served that a Zn/Ti ratio of 1.90/1 produced "pure" Zn_2TiO_4, i.e., a reflec-
tance spectra revealing no free ZnO or TiO_2. As shown in Figures 10 and 11, a
ZnO "knee" is observed at a Zn/Ti ratio as low as 1.95/1 for 900°C calcined
pigments, and at a Zn/Ti ratio of 2.00/1 for 1200°C calcined pigments. The
current program was designed to continue stoichiometry studies to fully char-
acterize the effects of various Zn/Ti ratios on optical properties of Zn_2TiO_4.

3.4.1 Pigment Preparation

Zinc orthotitanate powders having Zn/Ti ratios of 1.85/1, 1.90/1, 1.95/1,
2.00/1, and 2.05/1 were prepared by the MOX method. Mixtures of zinc oxalate-
"TiOX" compositions were dry-blended in polypropylene containers using nylon
balls. A 500°C/2 hr precalcination was followed by final reaction at 900°C/2
hr or 1050°C/2 hr, using the flash calcination method of direct insertion of
the powder into a furnace at temperature followed by removal to room tempera-
ture conditions. This method minimizes heat-up and cooldown that can add to
an undesirable increase in particle size due to sintering. A flow diagram
showing the processing appears in Figure 12.

A summary of gravimetric and X-ray analysis appears in Table 3. A com-
parison of actual weight percent residue versus theoretical reveals a somewhat
greater departure at the 1.95/1 2.00/1 and 2.05/1 stoichiometries. However,
these differences between actual and theoretical are all quite small, and no
particular significance is suggested by these data.
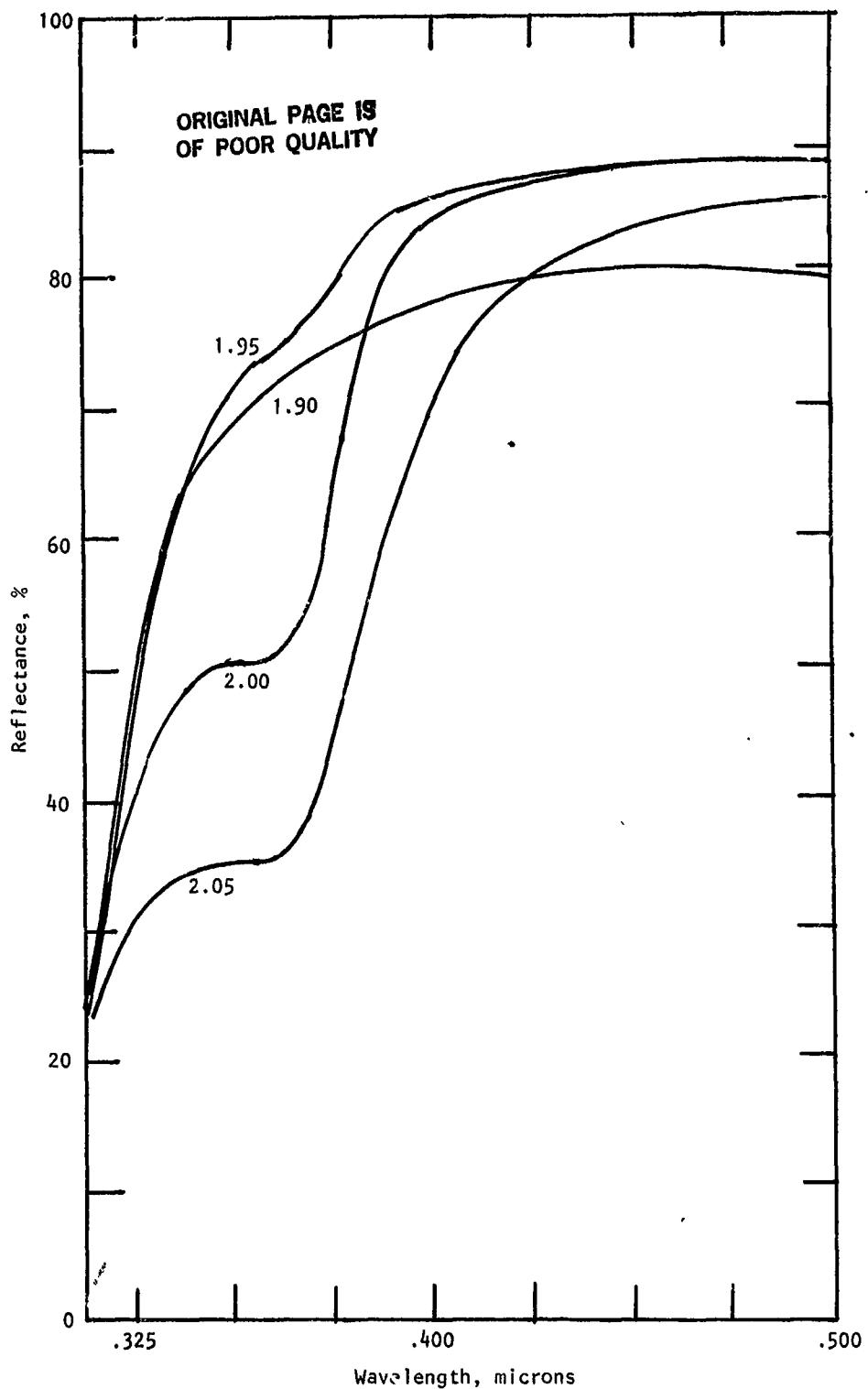
Figure 10. Reflectance spectra of Zn_2TiO_4 pigments calcined at 900°C, prepared at various Zn/Ti ratios.
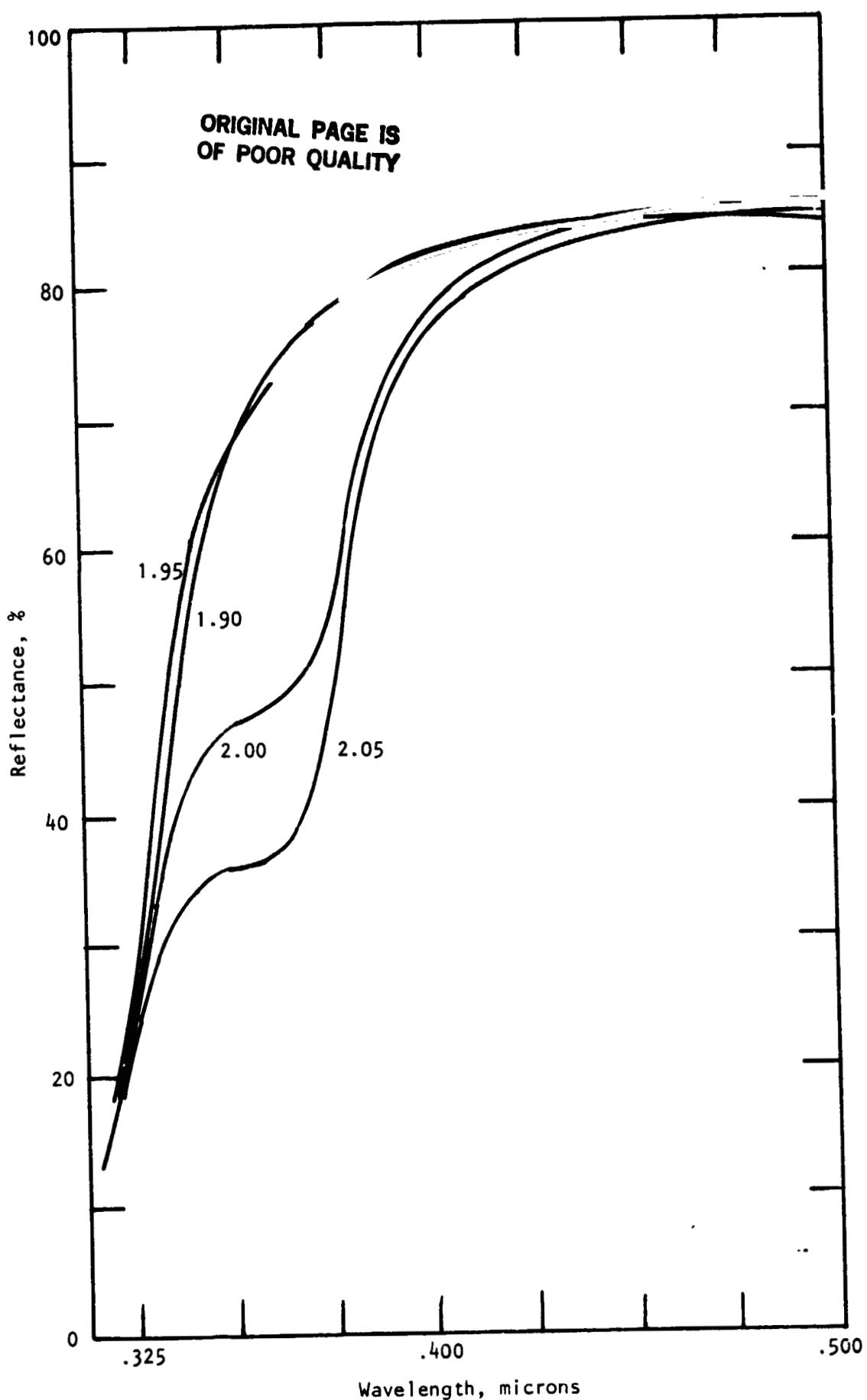
Figure 11. Reflectance spectra of Zn_2TiC_4 pigments calcined at $1200°C$, prepared at various Zn/Ti ratios.

Designation	Zn/Ti Ratio
MOX-85	1.85/1
MOX-90	1.90/1
MOX-95	1.95/1
MOX-00	2.00/1
MOX-05	2.05/1

MOX-85

500°C/2 hr

MOX-85(5)

900°C/ 2 hr   1050°C/2 hr

MOX-85(5-9)   MOX-85(5-10.5)

Acetic acid leach
80°C/1 hr

MOX-85(5-9-A)   MOX-85(5-10.5-A)

900°C/2 hr   1050°C/2 hr

MOX-85(5-9-A-9)   (MOX-85(5-10.5-A-10.5)
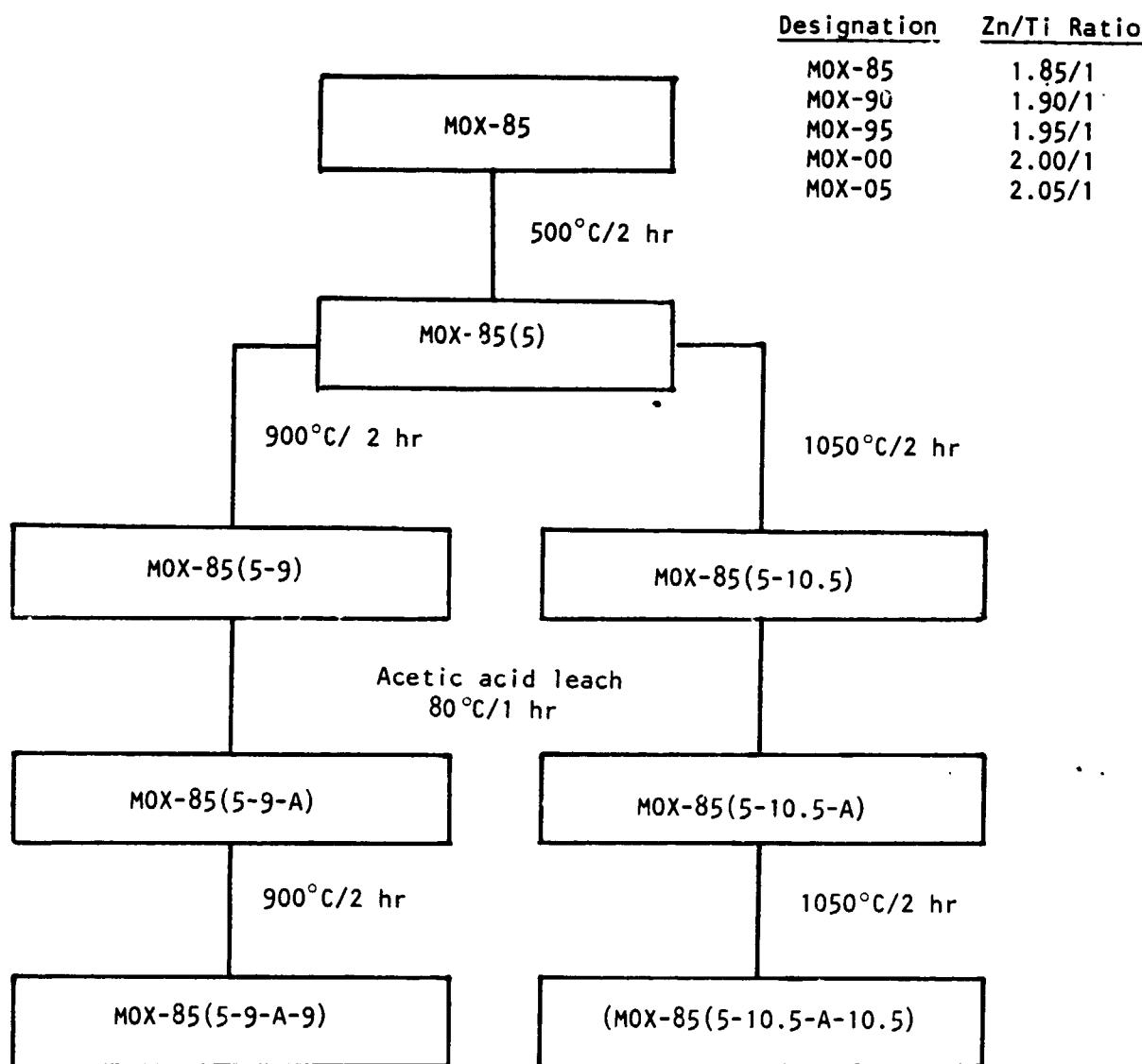
Figure 12.   Flow diagram for Zn_2TiO_4 syntheses and nonmenclature in
stoichiometry studies.

TABLE 3. SUMMARY OF GRAVIMETRIC AND X-RAY ANALYSES OF STOICHIOMETRY SAMPLES

Sample Designation	Calcination Conditions	Weight % Residue		Phases Present (X-ray)
		Actual	Theoretical	
MOX-85(5)	500°/2 hr	47.30		$ZnO + TiO_2(a)$*
MOX-85(5-9)	500°C/2 hr + 900°C/2 hr	46.92		Zn_2TiO_4
MOX-85(5-10.5)	500°C/2 hr + 1050°C/2 hr	46.64	46.65	Zn_2TiO_4
MOX-90(5)	500°C/2 hr	47.16		$ZnO + TiO_2(a)$*
MOX-90(5-9)	500°C/2 hr + 900°C/2 hr	46.81		Zn_2TiO_4
MOX-90(5-10.5)	500°C/2 hr + 1050°C/2 hr	46.66	46.58	Zn_2TiO_4
MOX-95(5)	500°C/2 hr	46.88		$ZnO + TiO_2(a)$*
MOX-95(5-9)	500°C/2 hr + 900°C/2 hr	46.45		Zn_2TiO_4
MOX-95(5-10.5)	500°C/2 hr + 1050°C/2 hr	46.08	46.51	Zn_2TiO_4
MOX-00(5)	500°C/2 hr	46.82		$ZnO + TiO_2(a)$*
MOX-00(5-9)	500°C/2 hr + 900°C/2 hr	46.34		Zn_2TiO_4
MOX-00(5-10.5)	500°C/2 hr + 1050°C/2 hr	46.13	46.45	Zn_2TiO_4
MOX-05(5)	500°C/2 hr	47.18		$ZnO + TiO_2(a)$*
MOX-05(5-9)	500°C/2 hr + 900°C/2 hr	45.93		Zn_2TiO_4
MOX-05(5-10.5)	500°C/2 hr + 1050°C/2 hr	46.02	46.39	Zn_2TiO_4

*Anatase.

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X-ray analyses revealed the same phase(s) at the different calcination temperatures, regardless of stoichiometry. Zinc oxide and anatase titania were in evidence in the 500°C material, while Zn_2TiO_4 was the only phase present in the 900°C and 1050°C powders. No ZnO excess was revealed in the X-ray studies.

3.4.2 Optical Studies

The various samples in Table 3 were prepared as powder compacts for optical analysis. In this method, the powder sample is poured into a copper ring which is placed on a flat clean surface. A close-fitting steel disk is inserted into the copper ring over the powder, and a pressure of 10 000 psi is applied. The compacted sample is held in place by this disk and a lip on the copper ring as depicted in Figure 13.

The more commonly used water spray method consists of spraying a water slurry of the powder sample onto a heated substrate such that the water is rapidly volatilized, leaving behind a coherent thin powder film for optical analysis. The advantage of the powder compact technique over the water spray method is that the sample thickness is about 1/8 in., thus eliminating substrate show-through influences on reflectance which can occur with thin coatings.

Optical spectra in the 0.3 to 0.5 micron wavelength region for the samples are shown in Figures 14 and 15. Among the powders calcined at 900°C (Figure 14), a trend toward ZnO formation with increasing Zn/Ti ratio can be observed; a similar trend is revealed for the 1050°C powders. This correlates with earlier work in which a ratio of 1.90 was shown to yield a powder free of ZnO or TiO_2 as determined from reflectance curves.

There is a question as to whether the "real" zinc orthotitanate does indeed exist as a $Zn_{1.90}TiO_4$ composition. The good correlation between actual vs. theoretical weight losses (Table 3) indicates that there is no preferential loss of either the zinc or titanium phase. Also, extensive calcination experimentation with zinc oxalate and "TiOX" have established predictable, reproducible weight losses, such that the precursor stoichiometry should be quite accurate. Both of these experimental findings would suggest that the Zn/Ti ratio of 1.90 is valid.

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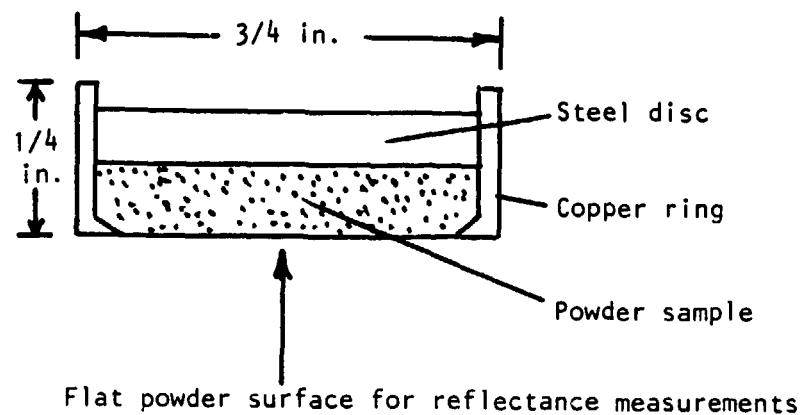
Figure 13. *Powder compact specimen for optical analysis.*
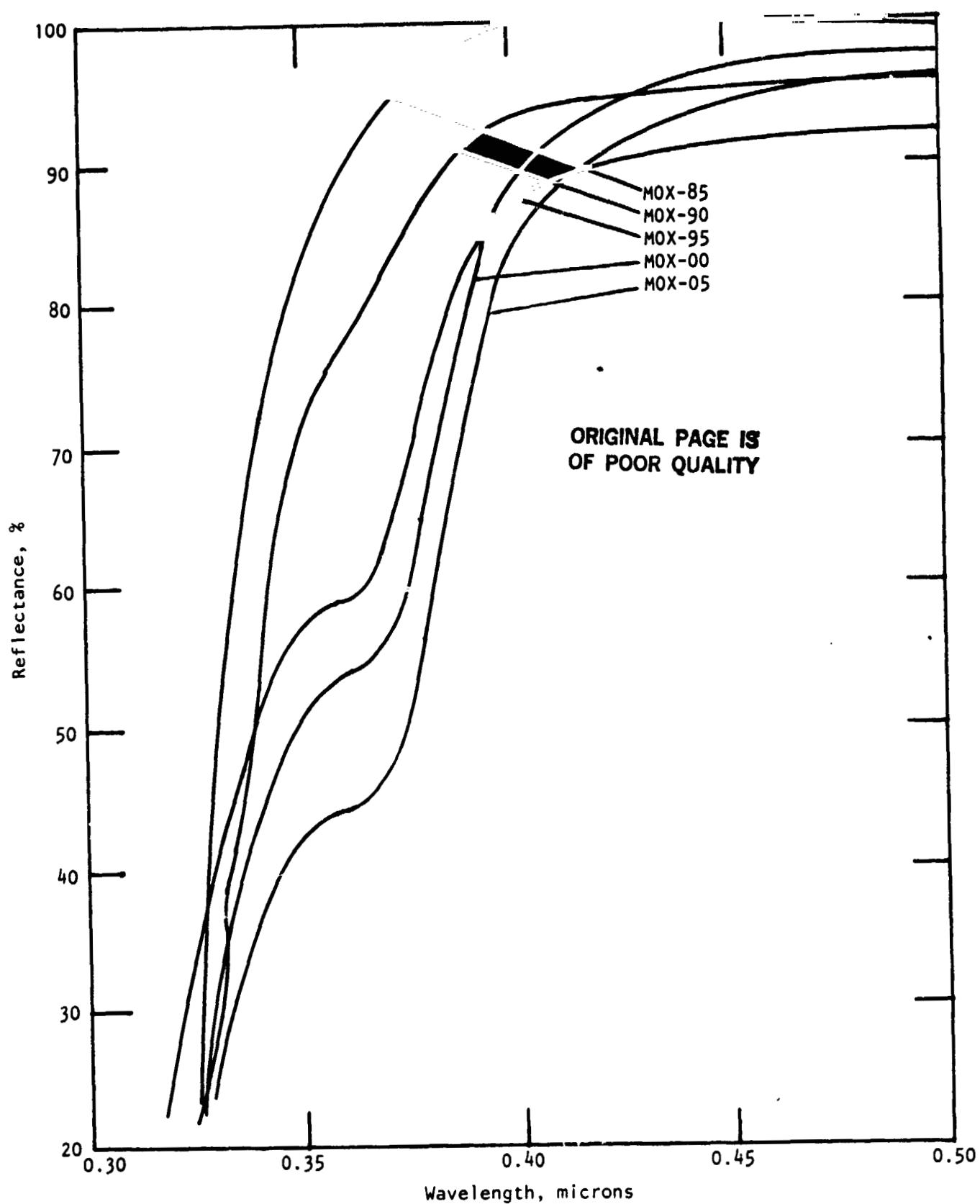
Figure 14. *Reflectance vs. stoichiometry for Zn_2TiO_4 powders calcined at $900°C$.*

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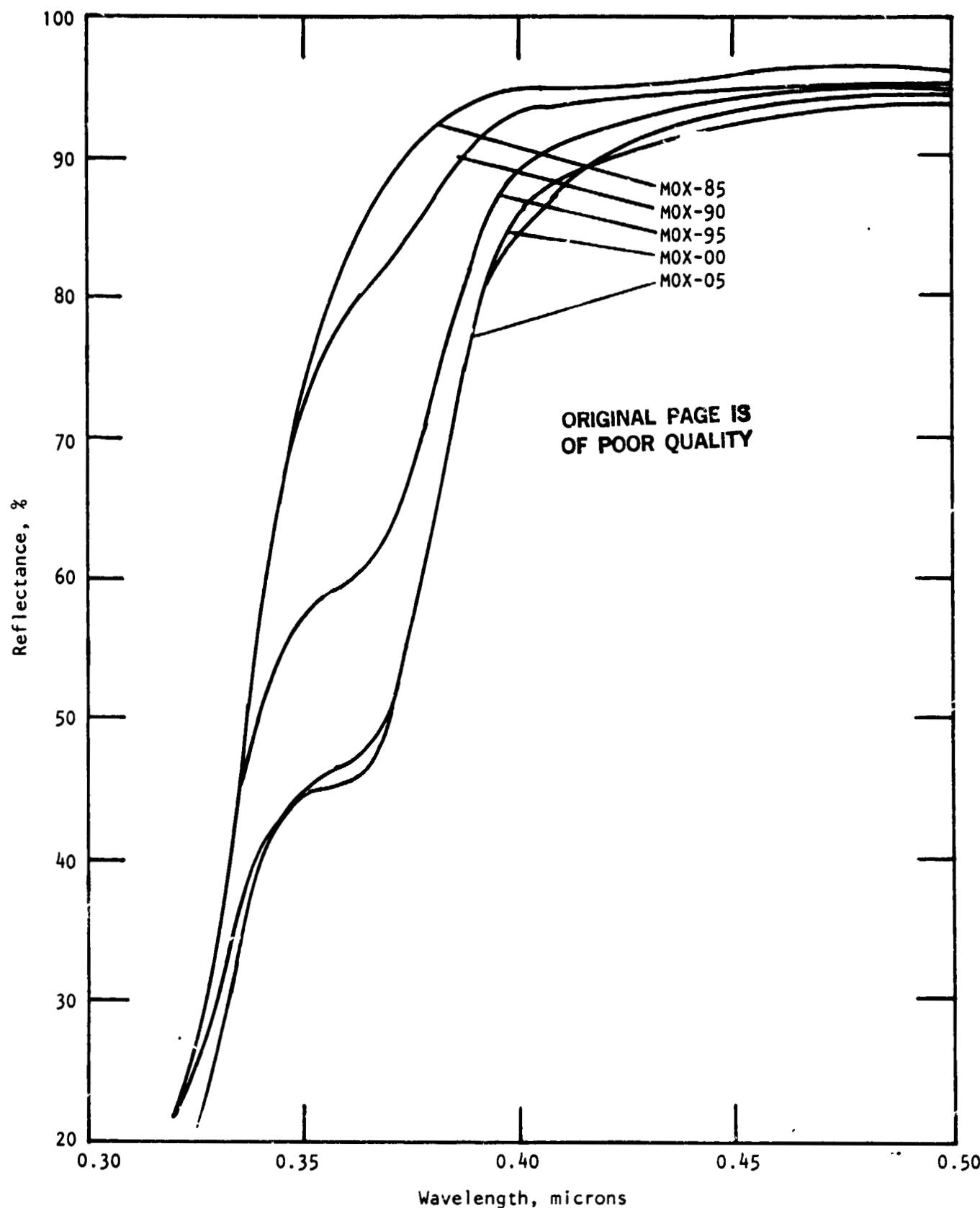
Figure 15. *Reflectance vs. stoichiometry for* Zn_2TiO_4 *powders calcined at* $1050^\circ C$.

Listed in Table 4 are selected reflectance values for the present materials along with those from a previous study. The $R_{.35}$ values which indicate the "knee" position decreases with increasing Zn/Ti ratios. Of particular significance is the fact that the $R_{.45}$ values for the present materials are higher than those for the previously made powders, i.e. >90% vs. <90%. This may be due to the fact that the present samples are quite thick and would not be subject to substrate show-through. The important consideration is that the potential α_s achievable is quite low and is probably less than 0.10 for the pigment alone.

3.4.3 Acid Leach Studies

A series of materials prepared with varying stoichiometries on a previous contract were subjected to an acetic acid leach in an effort to remove any free ZnO. This processing consists of digestion, with stirring, in a 50% acetic acid solution at 80°C for 1 hr. After filtering and drying, the resultant powder was calcined at 900°C for 2 hr to remove any residual acetate species.

As shown in Table 5, both gravimetric and optical analyses show that such removal was accomplished. Interestingly, gravimetric analyses showed a 2.3% weight loss for sample No. 1.90(6-9) and a 3.6% weight loss for sample No. 1.95(6-9), both of which revealed no ZnO excess in the optical spectra before acid leaching.

The reflectance curves for all of the acid leached samples were essentially identical as indicated by the $R_{.35}$ and $R_{.45}$ values in Table 5. The higher $R_{.45}$ values for the acid leached samples vs. the non-acid leached can be attributed to thickness i.e. powder compact vs. water sprayed, as discussed earlier in Section 3.4.2.

If the assumption is correct that ZnO is the only species soluble in acetic acid then it is clear that free, unreacted zinc oxide exists even in a 1.90 Zn/Ti material which should be rich in Ti. An implication for practical use is that materials of stoichiometries up to 2.05 Zn/Ti appear to oe converted to a 1.90 ratio material through acid leaching. Thus, this type of chemical extraction could be an additional processing step in obtaining the identical, high reflectance material, if slight stoichiometry errors were introduced earlier in the Zn_2TiO_4 production.

TABLE 4. REFLECTANCE AT .35 AND .45 MICROMETERS
FOR STOICHIOMETRY SAMPLES

Zn/Ti Ratio	MOX-(5-9) $R_{.35}$	$R_{.45}$	MOX-(5-10.5) $R_{.35}$	$R_{.45}$	MOX-(5-9)* $R_{.35}$	$R_{.45}$
1.85/1	85.0	100.0	75.5	96.0		
1.90/1	69.5	95.5	72.5	95.0	69.0	79.5
1.95/1	56.5	91.5	57.5	94.5	71.5	88.0
2.00/1	50.0	96.0	45.0	93.0	50.2	87.8
2.05/1	42.0	94.0	44.0	94.5	35.5	83.6

[a]Earlier studies.[3]

TABLE 5. EFFECT OF ACETIC ACID LEACH ON Zn_2TiO_4 POWDERS

Zn/Ti Ratio	Before Acid Leach $R_{.35}$	$R_{.45}$	After Acid Leach $R_{.35}$	$R_{.45}$	Weight Loss, %
1.90	69.0	79.5	67.0	93.0	2.28
1.95	71.5	88.0	66.5	93.0	3.60
2.00	50.2	87.8	72.0	94.0	3.95
2.05	35.5	83.6	66.5	93.5	5.56

Note: Reflectance values before acid leach made on water
spray samples, and after acid leach on compact samples.

The powder samples of varying stoichiometries (Table 3) were subjected to a hot acetic acid leach to remove free zinc oxide. The results of gravimetric analysis are presented in Figure 16 and show the following:

1. Increased material (ZnO) removal with increasing zinc-to-titanium ratio.

2. Less material removal for 1050°C calcined powder as compared to 900°C powder, indicating greater completeness of reaction at 1050°C.

3. Data for 900°C/8 hr powder similar to that for 1050°C/2 hr powder. Greater material removal for 900°C/2 hr powder shows less completeness of reaction at the shorter (2 hr) calcination time.

3.5 EFFECT OF SYNTHESIS TEMPERATURE

3.5.1 Low Temperature Synthesis: 600°-800°C

A series of calcinations were conducted at 600°-800°C to determine if Zn_2TiO_4 can be fully formed at lower temperatures. i.e. driving to completion the $ZnO + TiO_2$ reaction by using longer reaction times. The use of lower temperatures should result in products of finer particle size and, thus could provide higher reflectance materials.

The results of gravimetric and X-ray analyses for these materials are shown in Table 6. The weight percent residue values decrease very slightly with increasing calcination temperature, and all are quite close to the theoretical value.

X-ray analysis using powder pattern techniques showed the presence of Zn_2TiO_4 and ZnO in the powders calcined at 600°C. The line intensity in the X-ray pattern indicates an approximate composition of 60% Zn_2TiO_4-40% ZnO. No TiO_2 lines were observed. At the 700°C and 800°C levels, all samples exhibited patterns for Zn_2TiO_4 with no evidence of free ZnO. This indicates a level of about 5% or less of ZnO in these powders.

The reflectance spectra of the various powders were examined to determine to extent of the $ZnO + TiO_2$ reaction as indicated by $R_{.35}$. The data tabulated in Table 7 and graphically represented in Figure 17 show relatively low $R_{.35}$ values which increase as a function of both temperature and reaction time.

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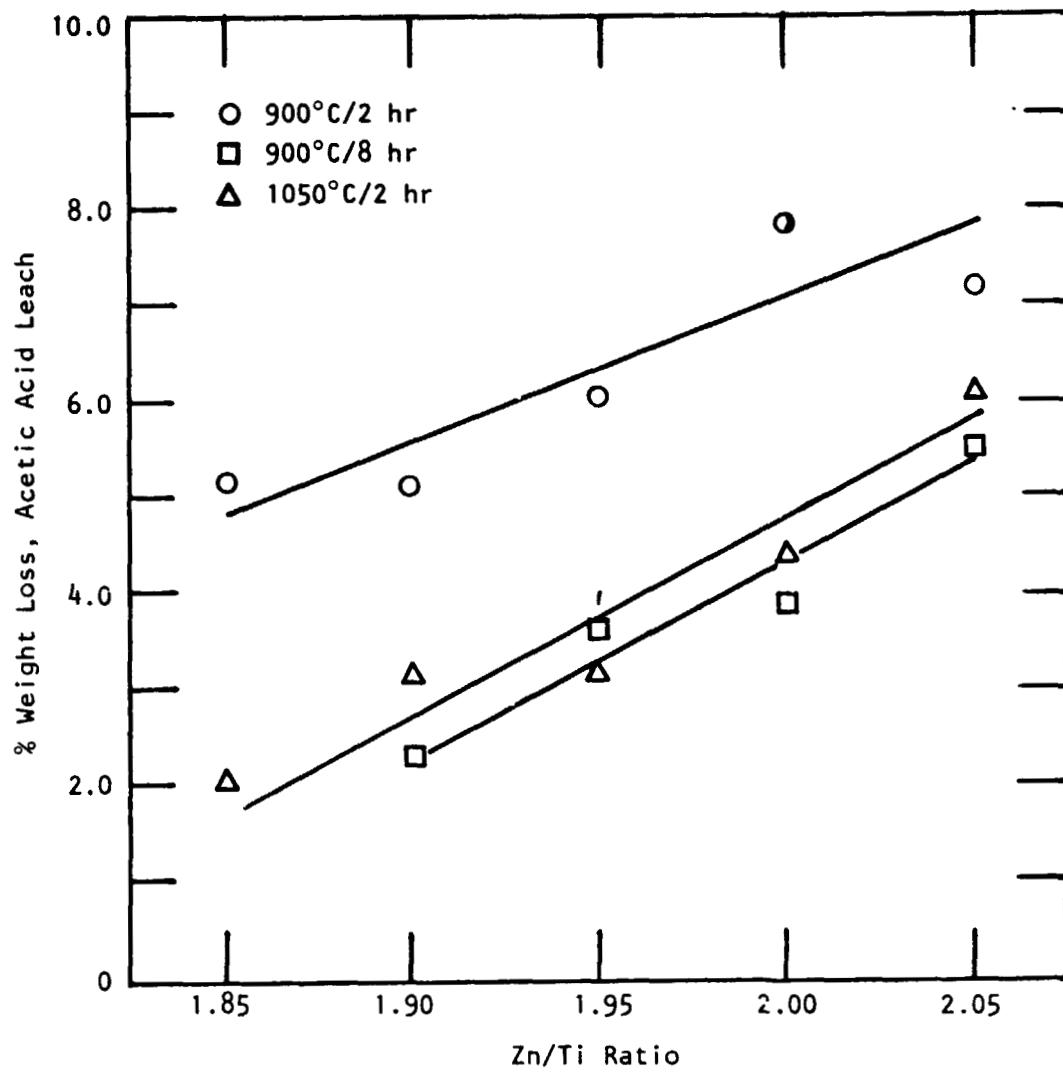
Figure 16. Zinc oxide removal on acid leaching of Zn_2TiO_4 as a function of Zn/Ti ratio and calcination conditions during synthesis.

TABLE 6. SUMMARY OF LOW TEMPERATURE SYNTHESIS OF Zn_2TiO_4

Sample Designation	Calcination Temp., °C	Time, hr	Weight & Residue Actual	Theoretical	X-Ray Analysis
MOX-00(6/8)	600	8	46.67	46.45	Zn_2TiO_4 + ZnO
MOX-00(6/16)	600	16	46.76	46.45	Zn_2TiO_4 + ZnO
MOX-00(7/8)	700	8	46.38	46.45	Zn_2TiO_4
MOX-00(7/16)	700	16	46.41	46.45	Zn_2TiO_4
MOX-00(8/2)	800	2	46.32	46.45	Zn_2TiO_4
MOX-00(8/8)	800	8	46.35	.46.45	Zn_2TiO_4
MOX-00(8/16)	800	16	46.35	46.45	Zn_2TiO_4

TABLE 7. REFLECTANCE OF Zn_2TiO_4 POWDERS
SYNTHESIZED AT 600°-800°C

(Zn/Ti Ratio = 2.0/1.0)

Calcination Conditions Temp., °C	Time, hr	Rλ .35	.50	1.00	$R_{.35}/R_{.50}$ x 100
600	8	15.0	97.0	97.5	15.5
	16	23.0	94.5	99.0	24.3
700	8	--	--	98.5	--
	16	43.5	91.0	98.5	47.8
800	2	38.0	94.5	96.0	40.2
	8	47.0	96.0	96.0	49.0
	16	53.5	94.5	96.0	56.6
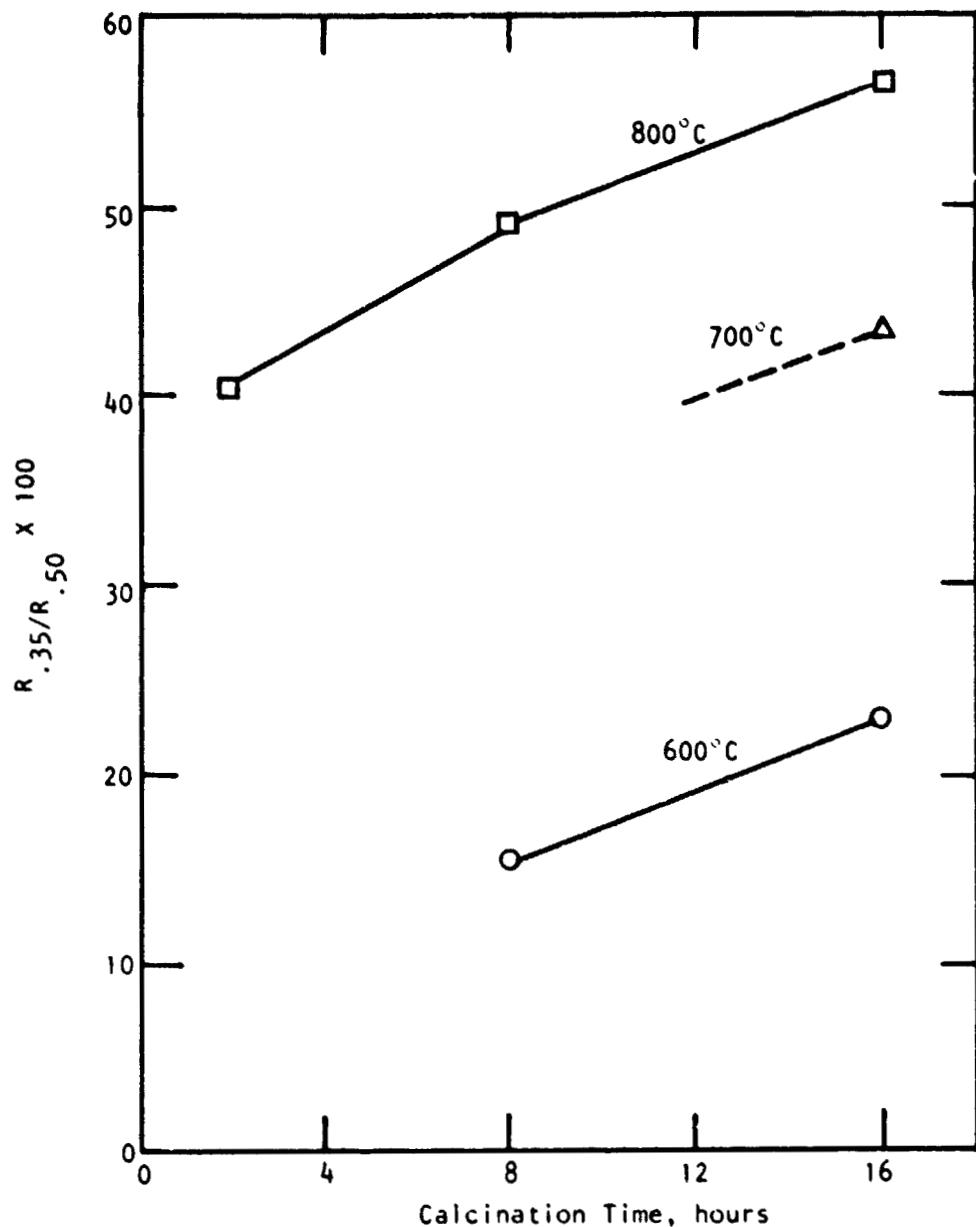
Figure 17. Reflectance at 0.35 micron vs. calcination time for Zn_2TiO_4 powders prepared at $600^\circ-800^\circ C$.

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The highest $R_{.35}$ values was shown by the 800°C/16 hr material; however, this value was lower than that for any comparable 2.0 Zn/1.0 Ti powders calcined at 900°C.

The peak reflectance ($R_{.50}$) values were not significantly higher than those for 900°C calcined pigments. Based on these results, the use of a calcination temperature lower than 900°C to synthesize Zn_2TiO_4 does not appear warranted.

3.5.2 Synthesis at 900°C

A series of Zn_2TiO_4 powders were prepared by calcination at 900°C for time periods from 1 to 16 hr. The matrix for these preparations is shown in Table 8, along with the results of gravimetric analysis. The data show no clear trend of increasing weight loss as a function of time, suggesting that the extent of reaction is essentially complete after 1 hr. It should be noted that the batch size was only 20 g each, and so the limited amounts of reactants assured completeness of reaction.

Representative reflectance values for these powders are presented in Table 9 and graphical representation of the $R_{.35}$ values is shown in Figure 18. The $R_{.35}$, or "knee" reflectance, is used to show the amount of free ZnO in the powders, i.e., lower values indicate greater amounts of ZnO.

It was anticipated that lesser amounts of ZnO would be observed with longer calcination times which would favor completeness of reaction. However, no such trend was observed at any of the stoichiometry levels. A puzzling aspect is that for the 1.95 and 2.00 Zn/Ti ratio materials, the $R_{.35}$ values suggest an increase in ZnO content with longer calcination times. These results indicate that the $ZnO + TiO_2$ reaction is essentially complete after 1 hr at a 900°C calcination temperature.

Another relationship shown in this study is $R_{.35}$ vs. Zn/Ti ratio. The $R_{.35}$ values were the highest at a 1.85 Zn/Ti ratio, with decreasing values at higher Zn/Ti ratios. This trend agrees with previous data of stoichiometry vs. $R_{.35}$.

A final observation is that the peak reflectance values at 0.5 micron were all quite high, indicating a potential for low α_s. The high reflectance also extends to the infrared wavelengths (note $R_{1.00}$ in Table 9). Reflectances of greater than 95% at 2 microns were observed for several of these samples.

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TABLE 8. WEIGHT PERCENT RESIDUE VS. CALCINATION TIME AT 900°C
IN PREPARATION OF Zn_2TiO_4 FROM PRECURSOR OXALATES

Zn/Ti Ratio	Weight % Residue After Given Calcination Time, (h)					Theoretical
	1	2	4	8	16	
1.85	46.29	46.18	46.40	46.39	46.20	46.65
1.90	46.31	45.99	46.02	46.03	46.04	46.58
1.95	46.19	46.22	46.22	46.20	46.21	46.51
2.00	46.19	46.24	45.26	46.18	46.15	46.45
2.05	45.91	45.91	45.71	45.88		46.39

TABLE 9. REFLECTANCE OF Zn_2TiO_4 POWDERS AS A FUNCTION
OF STOICHIOMETRY AND CALCINATION TIME AT 900°C

Sample Description		R_λ			$R_{.35}/R_{.50}$
Zn/Ti Ratio	Hold Time at 900°C, hrs.	$R_{.35}$	$R_{.50}$	$R_{1.00}$	x 100
1.85	1	81.0	97.0	96.0	83.5
	2	83.0	96.0	98.0	86.5
	4	82.0	96.0	98.0	85.4
	8	76.0	90.5	96.0	84.0
	16	82.0	97.0	98.0	84.5
1.90	1	80.0	96.0	99.0	83.3
	2	75.0	95.5	96.0	78.5
	4	--	--	96.0	--
	8	76.0	93.0	96.0	81.7
	16	76.0	96.0	97.0	79.2
1.95	1	65.0	94.5	96.0	68.8
	2	68.0	97.0	99.0	70.1
	4	69.0	98.0	96.5	70.4
	8	62.0	96.0	95.0	64.6
	16	54.0	96.5	97.0	56.0
2.00	1	65.0	98.0	99.0	66.3
	2	62.0	96.0	96.0	64.6
	4	57.0	93.5	95.0	61.0
	8	51.0	94.5	94.0	54.0
	16	59.0	93.0	96.0	63.4
2.05	1	60.0	97.0	98.5	61.9
	2	58.0	97.0	98.5	59.8
	4	57.0	97.0	98.5	58.5
	8	56.0	97.0	98.5	57.7
	16	57.0	97.0	99.0	58.8

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Zn/Ti Ratio
○ 1.85
△ 1.90
□ 1.95
▽ 2.00
⬡ 2.05

R.35/R.50 × 100

Calcination time, hours
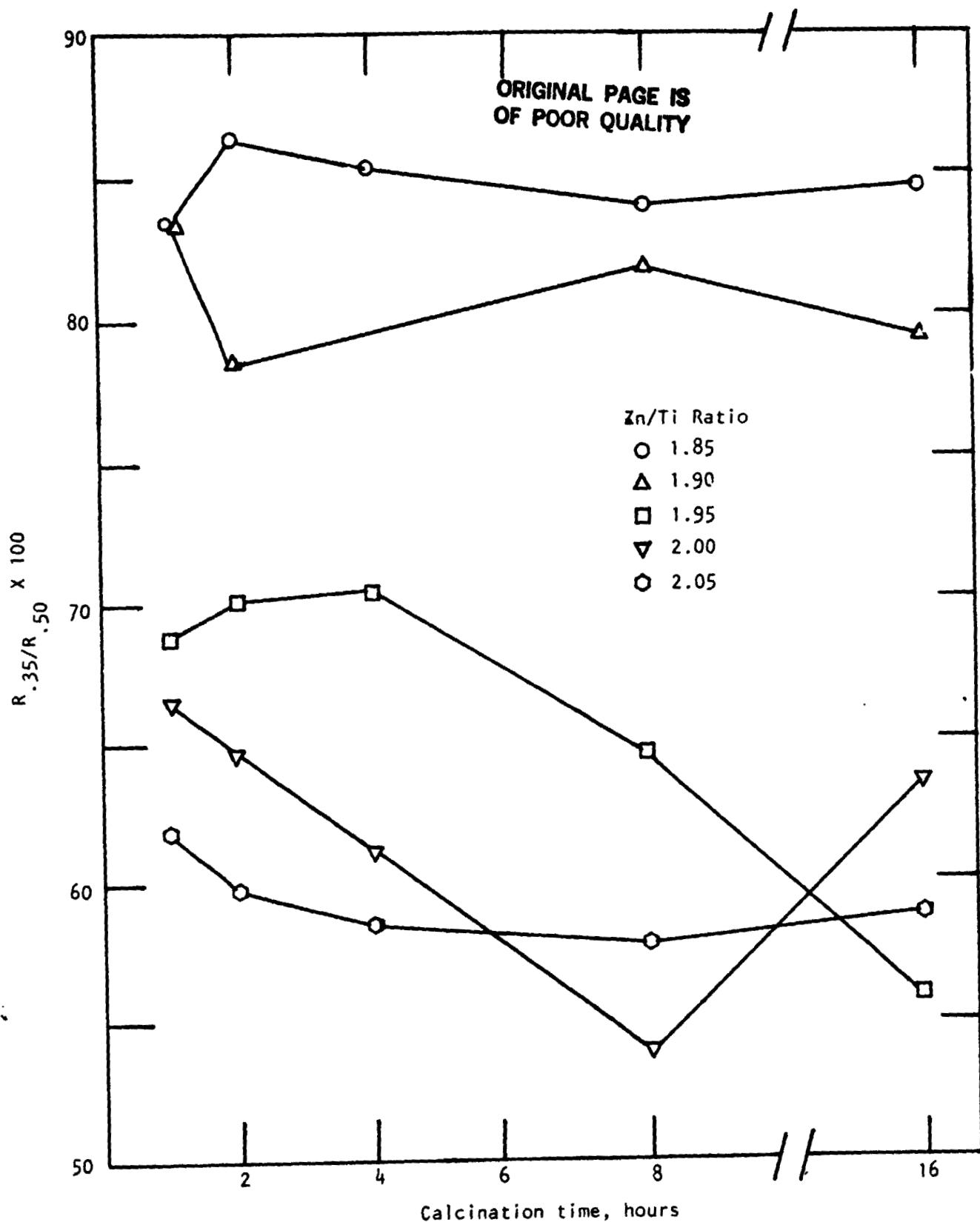
Figure 18. Reflectance at 0.35 micron vs. calcination time for Zn_2TiO_4 powders prepared at $900°C$.

3.6 SUMMARY

The synthesis of Zn_2TiO_4 was an ongoing function on this program. Whereas many of the earlier studies involved fairly small batches of up to about 20 g, the pigment needs on other programs as well as those for this contract indicated the need for scale-up. An increase in batch size to over 500 g was achieved during the course of this program. Zinc orthotitanate pigment of good uniformity can be reproducibly synthesized utilizing the process outlined in Table 1.

An additional finding in the current program is the need for close monitoring of precursor oxalate materials. Each oxalate batch is subjected to a calcination experiment in which gravimetric analysis is applied to the oxalate-to-oxide weight loss. In this manner, exact molecular weights are determined. The "TiOX" molecular weight has been observed to vary between about 142 to 148. The theoretical molecular weight of $Zn(C_2O_4 \cdot 2H_2O$ is 189.42. However, some zinc oxalate batches have exhibited molecular weights as low as about 172. This can be attributed to drying of the filtered precipitate at too high (>80°C) a temperature, such that some of the water of hydration was removed.

A result of the scale-up noted previously was the need for calcination times of 4 hr at 900°C to assure complete reaction. Such longer times may lead to particle growth, so that the finer particle size promised by the MOX process in small batch experiments is no longer as apparent. Thus the coprecipitation (COP) method appears to be a viable backup or alternative processing method for obtaining zinc orthotitanate pigment.

4. BINDER STUDIES

The initial choice in a binder material for this program was an organic silicone elastomer such as RTV 602 or RTV 615. After preliminary experiments had been conducted with these binders, a decision was made mutually between MSFC and IITRI personnel to have an inorganic silicate-bonded coating as the primary candidate for study. The reasons for this decision are discussed in the following sections.

4.1 POTASSIUM SILICATE BINDER

During the course of the studies to obtain a highly reflective and stable Zn_2TiO_4 pigmented thermal control coating, an inorganic silicate vehicle (as opposed to a polymeric silicone binder) was chosen for prime consideration. This choice is due to several desirable characteristics of silicate coatings: (1) lower solar absorptance, α_s; (2) higher emittance, ϵ; (3) greater stability in UV-vacuum; (4) no outgassing problems; and (5) higher electrical conductivity, minimizing charge buildup problems.

Historically, the objections to a silicate-bonded coating have been based on two disadvantages: (1) difficulties in spray technique to achieve a flaw-free, well-bonded coating; and (2) difficulty in cleanability. However the use of Z93 (silicate-bonded ZnO) on large areas of the Gemini early in the space program, on the radiators of the Apollo, and on the Skylab airlock module attests to its applicability. The cleanability problem may be circumvented through the use of protective polymeric films. Studies[12] at IITRI have shown that storage under plastics such as Mylar, Lexan, Type A Teflon, and Tedlar for periods up to 14 months maintains the excellent stability of Z93 to UN-vacuum.

4.2 SILICONE BINDER STUDIES

Binder studies at IITRI have included evaluation of PS7 potassium silicate (e.g., in Z93), RTV 602 methyl silicone (S-13G), and RTV 602 stripped (S13G/LO). The most recent work[3] has been concerned with Owens-Illinois 650

"Glass Resin." This binder would appear to be the most stable polymer to ultraviolet irradiation in vacuum.

The attempts to modify Owens-Illinois 650 "Glass Resin" were successful from the standpoint of eliminating "coasting." The modification process, however, apparently increases the outgassing potential of the modified (OI-650G) resin, seriously reducing its practical potential as a space stable binder. It should be used only in applications tolerant of contamination. The likelihood of developing an alternative process is extremely small. Degassing the modified resin in the B-stage in vacuo holds some promise but could be very expensive. Further complicating an objective appraisal of its merits are the facts that (1) the modified resin must be thermally cured; (2) like the unmodified resin, it too has a tendency to predispose the pigment to extensive S-band degradation; and (3) the ratio of trimethylchlorosilane/OI-650 must be carefully controlled within a very narrow range.

Based on these shortcomings of OI-650, it appeared desirable to investigate stripped RTV 602, which has been shown to exhibit acceptable outgassing behavior. This is a proven material and would ease the path toward achieving an engineering material. A second binder candidate would be RTV 615 methyl silicone. Mr. Wayne Slemp at NASA-Langley Research Center has reported the RTV 615 to be significantly more stable than RTV 602 to ultraviolet irradiation in vacuum. As was the case with RTV 602, modification of 615 to obtain low outgassing characteristics should be an achievable goal. The merits of RTV 615 as a paint binder, however, must be determined. Engineering studies which would evaluate its potential in this regard must be made to assure that it can meet the reasonable and applicable requirements such as those of NASA-MSFC Spec. No. 10 M01835 (for S-13G).

Experimentation with RTV 615 revealed certain characteristics of this binder material which can be summarized as follows:

1. Catalysis - RTV 615 does not cure with SRC-05 or with tetramethyl guanidene (used with RTV 602). A G.E. furnished catalyst termed RTV 615B effects a cure.

2. Curing - an elevated temperature (100°C/16 hr) has been found to be desirable for obtaining a tack-free film or paint.

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3. Solubility - the best single solvent appears to be toluene. Isopropyl alcohol is an assisting solvent but will not dissolve the polymer by itself. A previously used solvent (thinner) designated X-99 has been found to be an effective component. Its composition is: toluene 40%, isopropanol 20%, xylene 20%, butane 15%, and butyl acetate 5%.

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5. PAINT STUDIES

Paint formulations consist of three components: Zn_2TiO_4 pigment PS7 potassium silicate binder, and distilled water. Preparation and application of the Zn_2TiO_4 paint follow simple techniques quite similar to that for Z93. Preparation of paints consists of mixing of the components in a porcelain ball mill with porcelain balls for ~4 hr. Application of the paint is accomplished by spraying, using standard paint spray guns. The coating is applied as a continuous, wet film. This is permitted to dry until the gloss has almost disappeared, at which time the next coat is sprayed on. This is repeated until the desired thickness is achieved. The finished coating is cured by air drying, or can be baked at 120°C for complete water removal.

An important consideration in good bonding is preparation of the substrate to be coated. A chemical/mechanical process is used in which the surface is treated by techniques such as chemical etching or mechanical abrasion to obtain greater surface area for improved bonding. The surface is then cleaned with an alkaline detergent and rinsed with distilled water. The complete surface must be water break-free after the abrasion/cleaning process. By observing the above practices, excellent adhesion is achieved on metal surfaces.

During the course of this program, various means of optimizing the paint system were investigated. These studies included the effect of changes in pigment-to-binder ratio (PBR), in paint water content, and in curing conditions. These are discussed in the following sections.

5.1 PIGMENT-TO-BINDER RATIO (PBR)

The PBR for Z93 was fixed at 4.30 in early studies at IITRI.[4] It was determined that higher ratios for Z93 resulted in coatings which were somewhat soft, thus suggesting 4.30 as a maximum for good physical properties. Maximization of PBR was shown to be desirable for obtaining minimum α_s and maximum stability to a UV-vacuum environment.

Studies with Zn_2TiO_4 on this program explored higher PBRs up to 10.6. Early experiments considered ratios of 4.26, 4.73, and 5.32. As shown in Figure 19, an increase in reflectance with increasing PBR is observed, particularly at wavelengths of .35 and 2.0 microns.

Additional PBR experiments consisted of increasing the pigment loadings to 7.09, 8.51 and 10.64. Sprayability of these pigment-rich formulations was quite good. Examination of the 8.51 and 10.64 PBR cured coatings showed them to be somewhat softer than the 7.09 PBR samples. However, the integrity of these coatings appeared to be adequate; good bonding to the aluminum substrate was achieved.

For the balance of the program, a PBR of 7.1 was used as a good trade-off between optical and physical properties. It is possible that the higher pigment loadings may be used if the coatings are afforded adequate protection prior to launch.

5.2 WATER CONTENT STUDIES

Initial compositions of Zn_2TiO_4-silicate coatings were modeled after Z93 in total liquid content (Table 10). In preparing samples by the spray technique, Z93 samples were also prepared for comparison. Two differences were observed between Zn_2TiO_4 paints and Z93: (1) Zn_2TiO_4 compositions appeared to go on much "wetter" than did Z93; and (2) for the same number of spray cycles, more rapid thickness buildup was achieved with Z93.

The first difference was probably due to an excess of water content in the Zn_2TiO_4 mixtures. The Zn_2TiO_4 powder is coarser than calcined SP-500 ZnO and requires less water to achieve a sprayable viscosity. The second difference may also be traceable to the excess water in the Zn_2TiO_4 mixtures. The "wet" appearance which signals the end of a spray cycle was achieved more rapidly with Zn_2TiO_4 resulting in a lesser amount of coating per spray cycle. Thus, a decrease in water content and modification of spray technique were indicated as requirements to achieve coating thickness buildup with Zn_2TiO_4-silicate paints.

Additional studies involved compositions of lower liquid content as listed in Table 11. Improved sprayability was shown by these compositions, and an even lower water content appeared feasible. Therefore, greater

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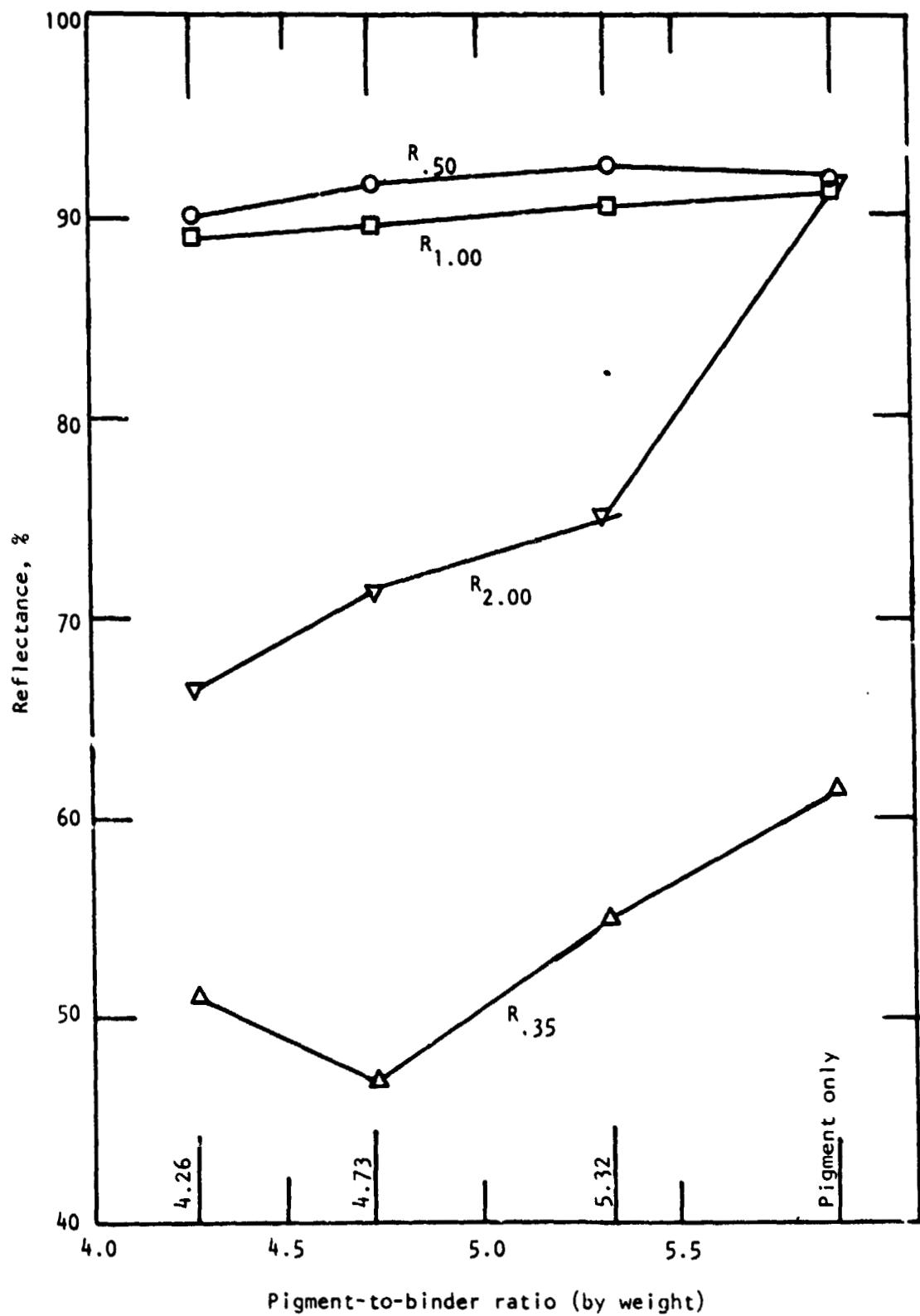
Figure 19. Reflectance of Zn_2TiO_4-silicate paints as a function
of pigment-to-binder ratio.

TABLE 10. PAINT COMPOSITIONS FOR SPRAYING STUDIES

Component	Composition for Given Pigment-to-Binder Ratio (PBR)		
	5.32	6.08	7.09
Zn_2TiO_4	40 g	20 g	20 g
PS7 (potassium silicate)	16 cc	7 cc	6 cc
H_2O	24 cc	13 cc	14 cc
Water content[a]	95 cc	95 cc	96 cc

[a]Based on 100 g pigment.

TABLE 11. PAINT COMPOSITIONS: DRY SPRAY MIXTURE

Component	Composition for Given Pigment to Binder Ratio (PBR)		
	4.26	5.32	7.09
Zn_2TiO_4	20 g	20 g	20 g
PS7 (potassium silicate)	10 cc	8 cc	6 cc
H_2O	7 cc	8 cc	10 cc
Water content[a]	78 cc	75 cc	76 cc

[a]Based on 100 g pigment.

reduction in water content to 56 cc H_2O was investigated. Compositions which were examined are listed in Table 12. In the spraying of these paints, compositions "A" and "B" showed good spraying characteristics while "C" went on very dry. The glossy appearance, which signals the end of a spray cycle with silicate paints, could only be achieved for "C" by a combination of opening the spray nozzle along with shortening the gun-to-substrate distance by about 50%.

Subsequent examination of cured coatings showed Series "A" and "B" to be uniform and smooth in appearance. In contrast, some of the "C" samples exhibited a very rough appearance which often results in "dry" spraying. Weight and thickness measurements showed that a heavier coating was achieved with fewer spray cycles for "C." A plot of coating thickness vs. weight (Figure 20) for various paints showed that "C" samples with the most uneven surface texture tended to be thicker for the same weight as compared to the other samples.

From these results, it would appear that a water content of about 66 cc per 100 g pigment is ideal for good sprayability along with achieving a good coating. This is in contrast with Z93 (silicate-bonded ZnO) for which 96 cc of total water is required for 100 g pigment, and can be attributed to the coarser particle size of Zn_2TiO_4 which requires lesser amounts of liquid for good wetting.

It should be noted, however, that the 66 cc H_2O per 100 g Zn_2TiO_4 applies for this particular batch of pigment. Slight variations from this ratio may be desirable, according to the pigment batch and, importantly, according to sprayer preference in viscosity.

5.3 OPTICAL STUDIES

The optical properties of samples with PBR varying from 7.09 to 10.64, along with variations in water content, were determined. These data are summarized in Table 13, and Figure 21 shows a plot of α_s as a function of coating thickness. These data show the following:

1. Maximum reflectance or minimum solar absorptance is achieved at a coating thickness of about 8 mils. This plateau is reached at about 5 mils for Z93.

TABLE 12. PAINT COMPOSITIONS[a]
FOR WATER CONTENT STUDIES

Component	Composition		
	A	B	C
Zn_2TiO_4	20 g	20 g	20 g
PS7	6 cc	6 cc	6 cc
H_2O	10 cc	8 cc	6 cc
Water content[b]	76 cc	66 cc	56 cc

[a]PBR = 7.09, Zn/Ti ratio = 1.95.

[b]Based on 100 g pigment.

TABLE 13. SOLAR ABSORPTANCE FOR Zn_2TiO_4-SILICATE COATINGS[a]

Sample No.	Solar Absorptance, α_s	Zn/Ti Ratio	PBR	Water Content,[a] cc	Thickness mils
LH-1-78	.178	1.95	7.09	75.9	3.1
LH-4-78	.108	1.95	7.09	75.9	6.8
LH-8-78	.125	1.95	7.09	75.9	5.7
LH-9-78	.214	1.95	7.09	66.0	2.2
LH-11-78	.120	1.95	7.09	66.0	5.3
LH-13-78	.118	1.95	7.09	66.0	6.4
LH-15-78	.126	1.95	7.09	66.0	~12
LH-16-78	.106	1.95	7.09	66.0	9.7
LH-17-78	.129	1.95	7.09	55.9	8.1
LH-19-78	.165	1.95	7.09	55.9	10.1
LH-22-78	.189	1.95	7.09	55.9	7.0
LH-23-78	.139	1.95	7.09	55.9	6.0
LH-27-78	.130	2.00	8.51	76.6	4.5
LH-29-78	.113	2.00	8.51	76.6	7.4
LH-33-78	.129	2.00	10.64	77.3	3.9
LH-36-78	.115	2.00	10.64	77.3	5.3

[a]Based on 100 g pigment.

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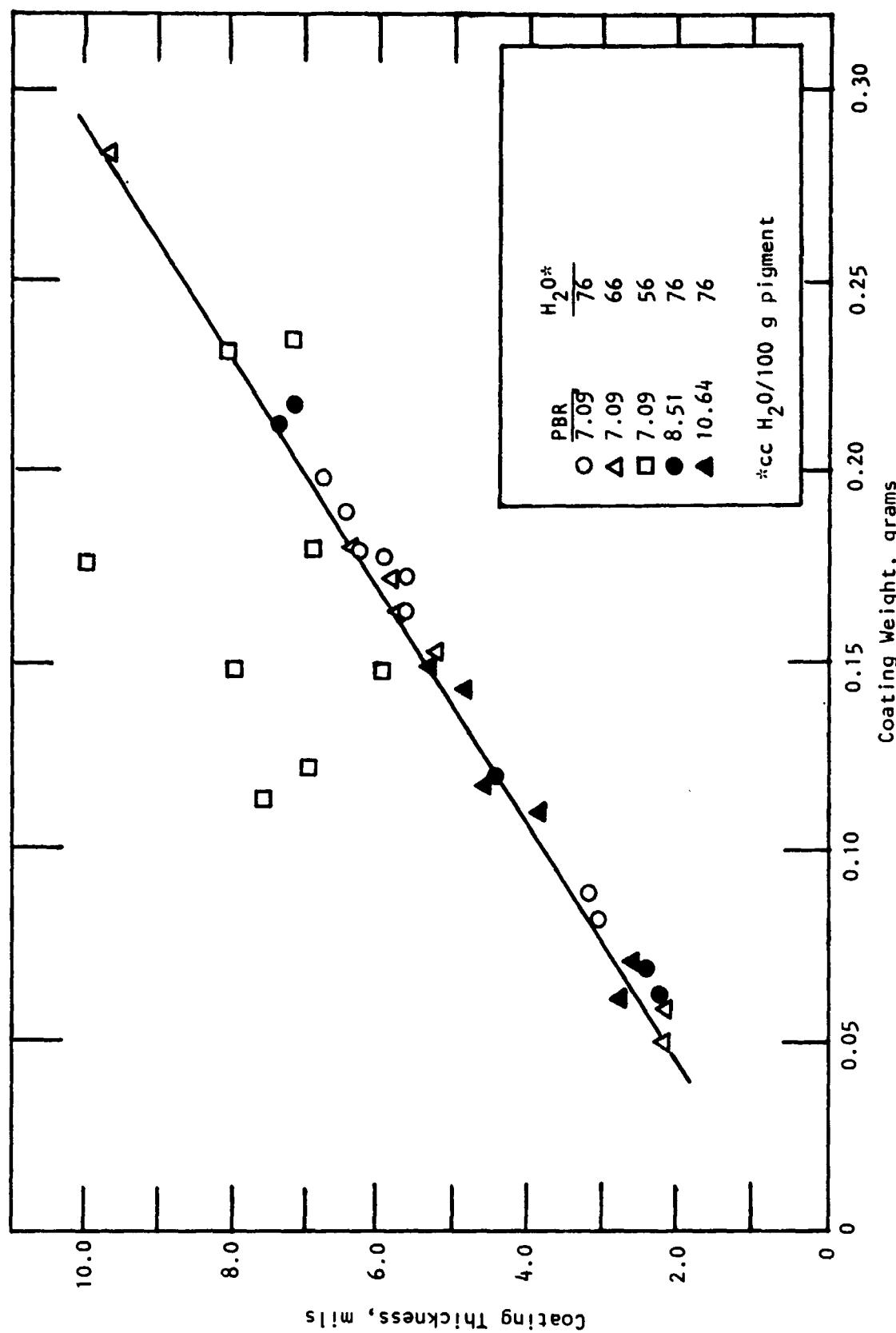
Figure 20. Coating thickness vs. weight for Zn_2TiO_4-silicate paints.
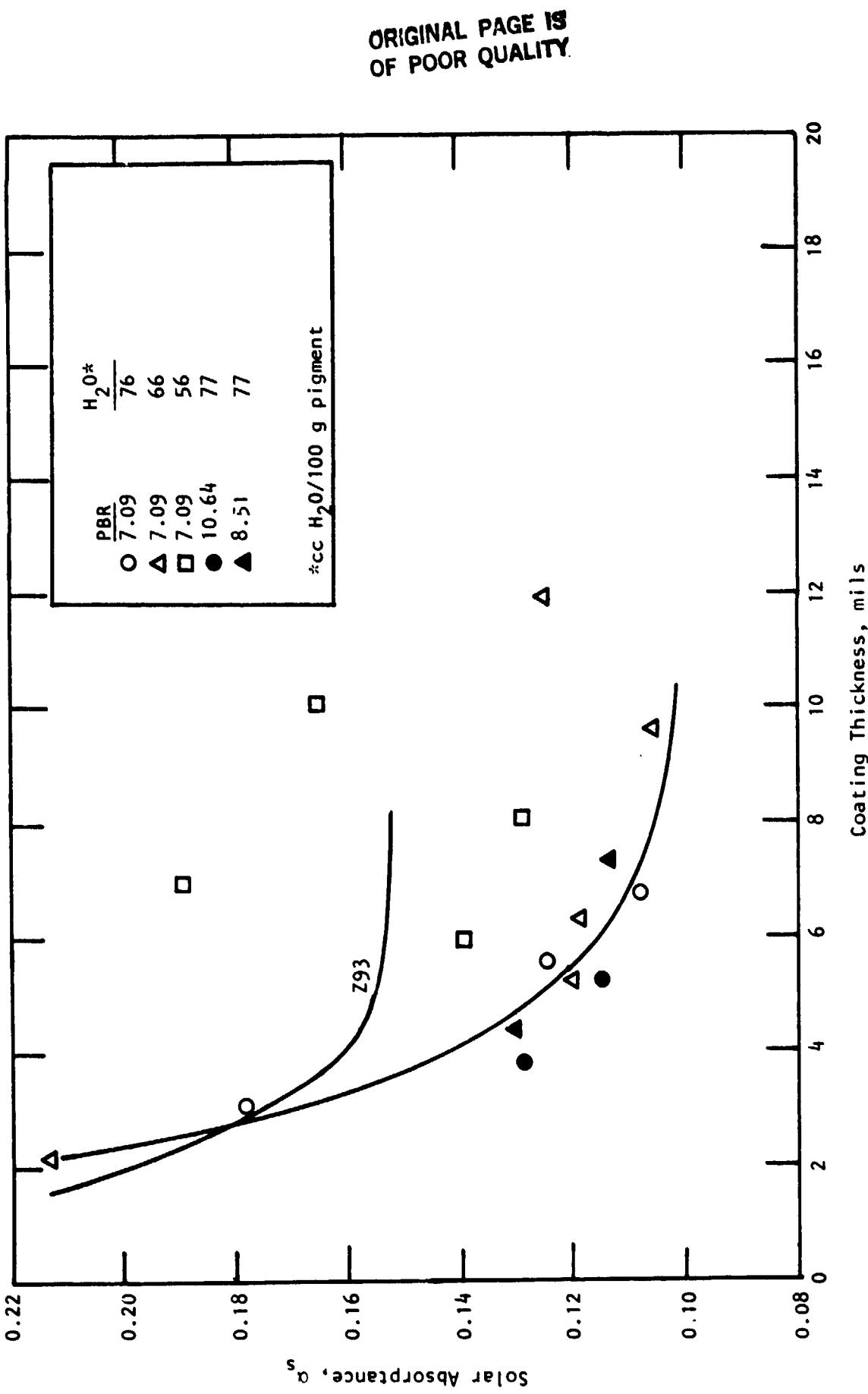
Figure 21. Solar absorptance vs. coating thickness for Zn_2TiO_4-silicate paints.

2. Samples with the lowest water content (56 cc H_2O/100g Zn_2TiO_4) exhibited higher α_s than the other samples. Poor spraying characteristics had been shown for these samples, resulting in rough, nonuniform surfaces.

3. Slightly lower α_s is indicated for samples with a PBR of 10.64 as compared to 7.09.

4. The lowest α_s observed was 0.106 for sample LH-16-78. Examination of the reflectance curve shows $R_{.35}$ to be about 64%; elimination of the free ZnO such that this value increases to about >80% would probably result in a α_s of lower than 0.10.

The total hemispherical emittance of zinc orthotitanate-silicate coatings has been determined to a temperature of -200°F in studies at Aerojet Electrosystems Co. As shown in Figure 22, the emittance decreases from a value of 0.91 at room temperature to a value of 0.84 at -220°F. This maintenance of ϵ_T at a fairly high level would make the use of Zn_2TiO_4 coatings attractive for cryogenic applications.

Some preliminary work was conducted on dual thermal control coatings, i.e., YB-71 coating on top of Z93, in an attempt to exploit the superior opacity of Z93. The results are shown in Table 14. The lowest solar absorptance value of 0.118 was shown by sample No. 6 which had a 5 mil Z93 coat covered with a 5.5 mil YB-71 top coat. The data show that thicker coatings of up to about 20 mils did not yield any higher reflectance. An important note is that, even at the high thicknesses, no cracking or physical deterioration was observed.

5.4 CURING STUDIES

Previous studies·have shown that Z93 (ZnO-silicate) is essentially completely cured after 24 hr. However, attempts to repair Zn_2TiO_4 coatings that had been cured for a period of 24 hr under ambient laboratory conditions resulted in complete loss of adhesion between coating and substrate. For this reason, a study was undertaken to determine the effects of cure time, temperature, and humidity on the adhesion of this coating to both metallic and fiberglass reinforced epoxy substrates.
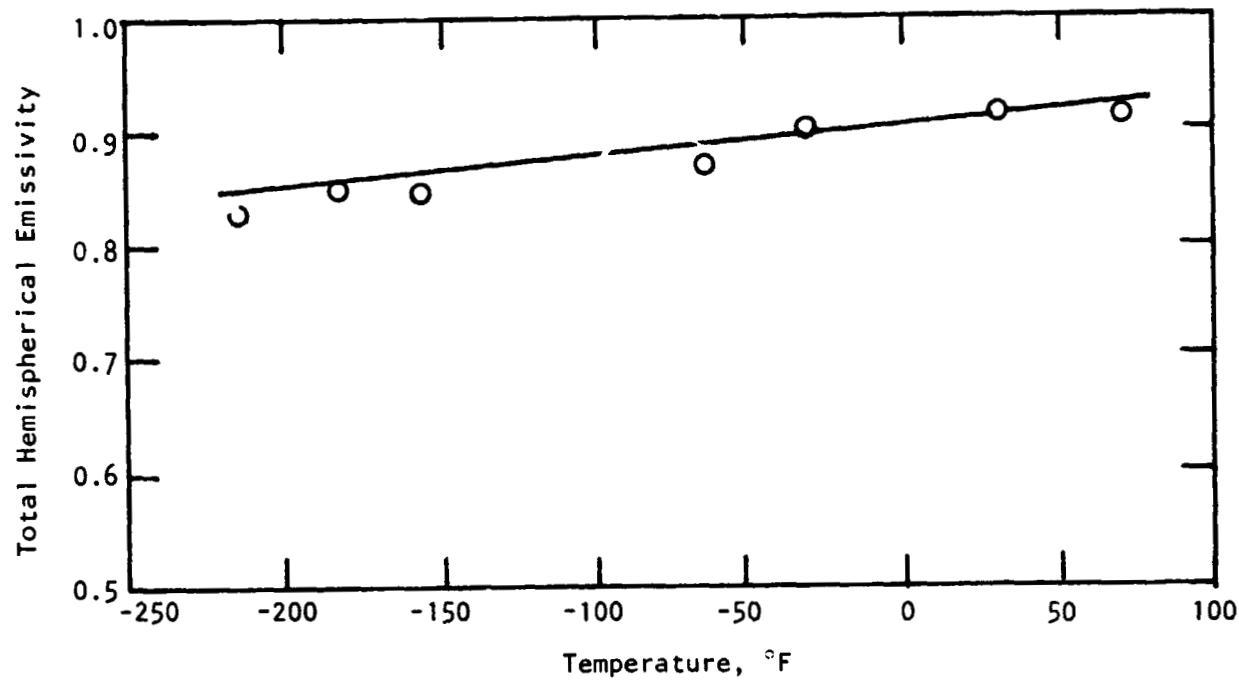
*Figure 22. Total hemispherical emissivity vs. temperature
for Zn_2TiO_4-silicate coating.*

TABLE 14. YB-71 ON Z93: DUAL
THERMAL CONTROL COATINGS

Sample No.	Thickness, mils			Solar Absorptance, α_s
	Z93	YB-71	Total	
1	5.0	6.0	11.0	.120
2	5.5	7.5	13.0	.118
3	6.0	7.0	13.0	.117
5	5.5	9.5	15.0	.121
6	5.0	5.5	10.5	.118
13	8.0	9.0	17.0	.121
21	6.0	9.5	15.5	.122
22	6.0	11.5	17.5	.126
23	7.0	12.5	19.5	.121
27	4.0	10.0	14.0	.123
28	4.5	11.0	15.5	.123
39	2.5	2.5	5.0	.139
50	2.0	3.5	5.5	.146
51	2.5	4.0	6.5	.141
52	2.5	5.0	7.5	.138
55	2.5	6.5	9.0	.135
56	2.5	5.5	8.0	.135
57	2.5	6.0	8.5	.138

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A series of 90 test specimens of aluminum (48), magnesium (12), and fiberglass-epoxy (30) measuring 2 in. x 4 in. were used in this study. Specimens were abraded with a No. 60 grit abrasive cloth and then washed with a 50/50 mixture of Alconox-Comet cleanser until a water break-free surface was obtained. The specimens were then rinsed with distilled water and air dried.

Just prior to spray coating all specimens were wiped with 200 proof alcohol. After coating with YB-71, the specimens were air-dried for 4 hr under ambient conditions, separated into groups of three, and then subjected to the cure conditions listed in Table 15.

After aging in ovens or at room temperature (65°-70°F) under two different humidity conditions, two specimens of each set or group were immersed in tap water (100°F) and observed for coating adhesion or loss of adhesion. If after 5 min immersion in water the coating did not slough off, the wet area was rubbed vigorously between thumb and forefinger to note pigment rub-off. If rub-off did not occur, the specimens were returned to the water bath and held for 30 min.

The results of accelerated curing at elevated (150°and 200°F) temperatures are shown in Table 16. Adequate curing had not occurred, even after 16 hr. Furthermore, the water test indicates deterioration in adhesion with increasing times at both 150° and 200°F.

Room temperature cure results (Table 17) show that a minimum of 7 days is required for adequate cure. A 14-day cure would appear to assure good curing of coatings. A high humidity environment is deleterious to curing properly.

5.5 SUMMARY

Various studies were conducted to determine formulation and application parameters which would yield a zinc orthotitanate-silicate paint of optimum physical and optical characteristics. The optimum paint to emerge from these studies has been designated YB-71, and the parameters for obtaining this material are as follows:

1. Pigment synthesized with a zinc-to-titanium ratio of 1.90 to 1.00 is to be used.

2. Pigment-to-binder (PS7 potassium silicate) ratio of 7.1 appears optimum for good optical and physical properties.

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TABLE 15. TEST MATRIX FOR A STUDY OF EFFECT
OF CURE CONDITIONS ON ADHESION
OF Zn_2TiO_4-SILICATE COATINGS

Time Period	Number and Type of Samples			
	Room Temperature		150°F	200°F
	50% RH[a]	90% RH[a]		
4 hr			3A	3A
8 hr			3A	3A
16 hr			3A	3A
1 day	3A, 3F	3A, 3F		
3 days	3A, 3F	3A, 3F		
7 days	3A, 3F, 3M	3A, 3F, 3M		
14 days	3A, 3F, 3M	3A, 3F, 3M		
28 days	3A, 3F	3A, 3F		

Note: A = aluminum, F = fiberglass, M = magnesium
substrates. Three (3) replications of each.

[a]RH = relative humidity, ±10%

TABLE 16. OVEN CURING OF COATED ALUMINUM SAMPLES

Time in Oven hr	Observations	
	150°F Curing Temperature	200°F Curing Temperature
4	Complete loss of adhesion within 4 min.	Complete loss of adhesion within 4 min.
8	Complete loss of adhesion within 2 min.	Complete loss of adhesion within 2 min.
16	Loss of adhesion after 1 min.	Slight adhesion exhibited for 2 min.

TABLE 17. CURING AT ROOM TEMPERATURE UNDER DIFFERENT HUMIDITY CONDITIONS

Days Aged	Sub-strate[a]	Observations 40-50% RH	90% RH
1	A	3 min, complete loss of adhesion	1 min, complete loss of adhesion
	F	1 min, adhesion lost	15 sec - adhesion lost
3	A	5 min, some pigment rub-off 27 min, no further rub-off	2 min, adhesion lost
	F	5 min, no rub-off 20 min, some rub-off at edges	30 sec, adhesion lost
7	A	5 min, slight turbidity in H_2O, slight rub-off 10 min, no further rub-off	1.5 min, adhesion lost
	M	5 min, no rub-off 10 min, no rub-off	30 sec, adhesion lost
	F	5 min, no rub-off 30 min, no rub-off	15 sec, adhesion lost
14	A	30 min, no rub-off	1 min, adhesion lost
	M	30 min, no rub-off	1 min, adhesion lost
	F	30 min, no rub-off	30 sec, adhesion lost
28	A	30 min, no rub-off	30 min, very slight rub-off
	F	30 min, no rub-off	30 min, no rub-off on one sample; however, on drying and subsequent coating shrinkage, coating delaminated from substrate; other sample, large section came off in one piece during rub test.

[a]A = aluminum, F = fiberglass, M = magnesium.

3. The water content in the paint formulation is approx-
    imately 66 cc H_2O per 100 g pigment. The exact
    amount is that which yields a mix of optimum spray
    viscosity

4. Curing should be conducted under ambient laboratory
    conditions for at least one week--preferably two
    weeks, for optimum adhesion.

5. A thickness of about 8 to 10 mils yields highest re-
    flectance and lowest solar absorptance. An α_s value
    of 0.10 is achievable.

6. ENVIRONMENTAL TESTING

UV-vacuum studies which were completed successfully on this program include two 1000 ESH (equivalent sun hours) tests and a 5000 ESH exposure. One of the 1000 ESH exposures was conducted at IITRI; the other 1000 ESH and the 5000 ESH exposures were performed at the Marshall Space Flight Center (MSFC).

6.1 TEST FACILITIES - IITRI

The IRIF, an acronym for "In-Situ Reflectance/Irradia'.on Facility" is a multiple-sample ultraviolet-simulation facility possessing in situ hemispherical spectral-reflectance-measurement capabilities. The basic measurement is that of diffuse spectral reflectance in the 220-to 2600 microns wavelength range. The facility incorporates an integrating sphere, patterned after one described by Edwards et al.,[14] and modified for use with the Beckman DK spectroreflectometers. The integrating spheres normally operate in vacuum. A sample transfer mechanism, during irradiation, maintains each sample in contact with a temperature-controlled sample table. The transfer under high vacuum of any sample to the integrating sphere for measurement and its subsequent return to the sample table for continued irradiation are routine operations. Pumping is conducted with a 400 liter/sec ion pump, and rough pumping is done with cryosorption pumps.

Standard operating procedure requires that, after pump-down, the sample be heated with warm water to remove gross volatiles (if any). Immediately prior to and during irradiation cold water is supplied to the sample cooling table. While still under high vacuum, diffuse spectral reflectance measurements are then taken of each of the test samples in the spectral range of 325-2600 microns. Such measurements are repeated after each prescribed test interval. UV irradiation rates are 6 suns at the sample location in IRIF tests, using an A-H6 source Its high ratio of ultraviolet to total (radiant) energy permits accelerated ultraviolet testing at several equivalent solar factors (based on total ultraviolet only) without substantial sample heating.

6.2 TEST FACILITIES - MSFC

The space simulation chamber at MSFC has as a solar source, a Hanovia 5000 watt Hg-Xe lamp which is unfiltered and unfocused. Acceleration factor is 3.5 suns. In situ reflectance measurement capability makes use of a computer-controlled DK-2 spectrophotometer. Samples are maintained at an ambient water temperature of $15°-20°C$ under a vacuum of 2×10^{-7} to 2×10^{-8} torr.

6.3 UV-VACUUM STUDIES

6.3.1 Test 1000 ESH (A)

The initial UV-vacuum stability test was conducted on a series of zinc orthotitanate-silicate paints with the following variables:

1. Stoichiometry - zinc to titanium ratios of 1.85, 1.90 1.95 2.00. and 2.05.

2. Synthesis temperature - 900° and 1050°C.

3. Acid leached pigments - washed in acetic acid to remove free ZnO, and refired at 900° or 1050°C to volatilize any residual contaminants.

4. Pigment-to-binder ratio of 4.30.

Tabular results for 900°C pigment paints tested at IITRI and for 1050°C pigment paints tested at MSFC are shown in Tables 18 and 19.

Perhaps the most significant observation is the good stability ($\Delta\alpha_{1000}$ ESH of about 0.01) shown by most of these silicate-bonded paints. Additionally, comparison of the $\Delta\alpha_{250}$ ESH and $\Delta\alpha_{1000}$ ESH data suggests that the bulk of the damage occurs at the shorter terms (250 ESH), and subsequent changes in reflectance appear to be minimal. Differences due to variations in stoichiometry or acid leaching are not obvious.

Examination of initial (unirradiated) optical data shows that the reflectance of the paint is considerably lower than that of tl pigment. A comparison of reflectance values at .50 mi ns (Tables 18 and 19) show differences of about 6 to 12%, with the paint always being less reflective than the corresponding pigment. It is possible that higher reflectance approaching that of the pigment alone may be reached by: (1) increased thickness; (2) higher pigment-to-binder ratio; and (3) use of a spray technique to maximize pigment concentration at the paint surface

TABLE 18. SUMMARY OF 1000 ESH TESTS ON PAINTS INCORPORATING PIGMENTS CALCINED AT 900°C

Sample	$R_{.50}$ Pigment	Paint	Solar Absorptance, αs Initial	176 ESH	1000 ESH	$\Delta\alpha_{1000}$ ESH
			5-9 Samples			
MOX-85	100	85.0	.218	.232	.232	.014
MOX-90	96.0	85.0	.222	.239	.239	.017
MOX-95	92.0	81.5	.242	.259	.259	.026
(b)		82.5	.252	.248	.278	.026
MOX-00	97.5	85.0	.210	.219.	.219	.009
MOX-05	96.0	86.0	.214	.227	.231	.017
			5-9-A-9 Samples			
MOX-85	--	89.0	.166	.176	.173	.013
MOX-90	--	89.0	.169	.182	.183	.014
MOX-95	--	86.0	.176	.197	.215	.039
(b)	--	87.5	.179	.188	.198	.019
MOX-00	--	37.5	.184	.209	.214	.030
MOX-05	--	89.0	.167	.186	.186	.019

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TABLE 19. SUMMARY OF 1000 ESH TESTS ON PAINTS
INCORPORATING PIGMENTS CALCINED AT 1050°C

Sample	$R_{.50}$		Solar Absorptance, α_s			$\Delta\alpha_{1000\ ESH}$
	Pigment	Paint	Initial	176 ESH	1000 ESH	
5-10.5 Samples						
MOX-85	96.0	86.5	.205	.211	.215	.010
MOX-90	95.5	86.0	.198	.204	.209	.011
MOX-95	95.0	88.5	.191	.203	.208	.017
MOX-00	94.5	89.0	.182	.188	.193	.011
MOX-05	93.5	88.0	.200	.207	.210	.010
5-10.5-A-10.5 Samples						
MOX-85	--	90.5	.168	.187	.196	.026
MOX-90	--	88.5	.185	.204	.211	.026
MOX-95	--	88.0	.186	.196	.206	.020
MOX-00	--	89.0	.166	.172	.180	.014
MOX-05	--	87.0	.201	.207	.211	.010

The results of UV-vacuum testing are summarized in Figure 23 for the 900°C pigment paints. No definite trend in stability as a function of stoichiometry, appears to exist for either the acid leached or untreated pigment coatings. For paints pigmented with 1050°C as-calcined powders (Figure 24) stability was similar for the various Zn/Ti ratio materials. The acid leached materials appeared less stable, especially for the lower Zn/Ti ratio paints. This may be explained in this manner: the lower Zn/Ti ratio has a higher proportion of a titanium component. Thus, acid leaching to remove free ZnO could yield a greater amount of free unreacted TiO_2, which can deleteriously affect stability.

Reflectance changes at particular wavelengths for both the IITRI and MSFC exposure for 1050°C pigment paints are shown in Table 20. A summary of these data appears in graphic form in Figure 25. These data points are obtained by adding the values of reflectance changes listed in Table 20.

Examination of the data in Figure 25 shows the following:

1. No particular trend in stability vs. stoichiometry is observed for the non-acid treated pigment paints.

2. A trend toward improved stability with increasing Zn/Ti ratio is apparent for the acid-leached pigment paints.

3. At Zn/Ti ratios of 1.85-1.95, the paints pigmented with non-acid leached pigments appear more stable than those incorporating leached pigments; at ratios of 2.00 and 2.05, this difference is not readily evident.

4. The IITRI data indicate somewhat better st   ty for the various paints as compared to the MSFC   ults.

6.3.2 Test 1000 ESH (B)

The results of a 1000 ESH test for various silicate-bonded Zn_2TiO_4 coatings are shown in Table 21. These data were generated in a test at MSFC. The following sample variables were examined in this test:

1. Pigment-to-binder ratios of 4.26, 5.32, and 7.09.

2. Pigment calcination temperatures of 900° and 1050°C.

3. Zn/Ti ratios for the pigment of 1.95 and 2.00.

As the data show, all samples exhibited excellent stability. Changes in α were all less than 0.01. In view of the   very limited $\Delta\alpha_s$ values, behavioral trends as a function of the above-listed variables were not evident.

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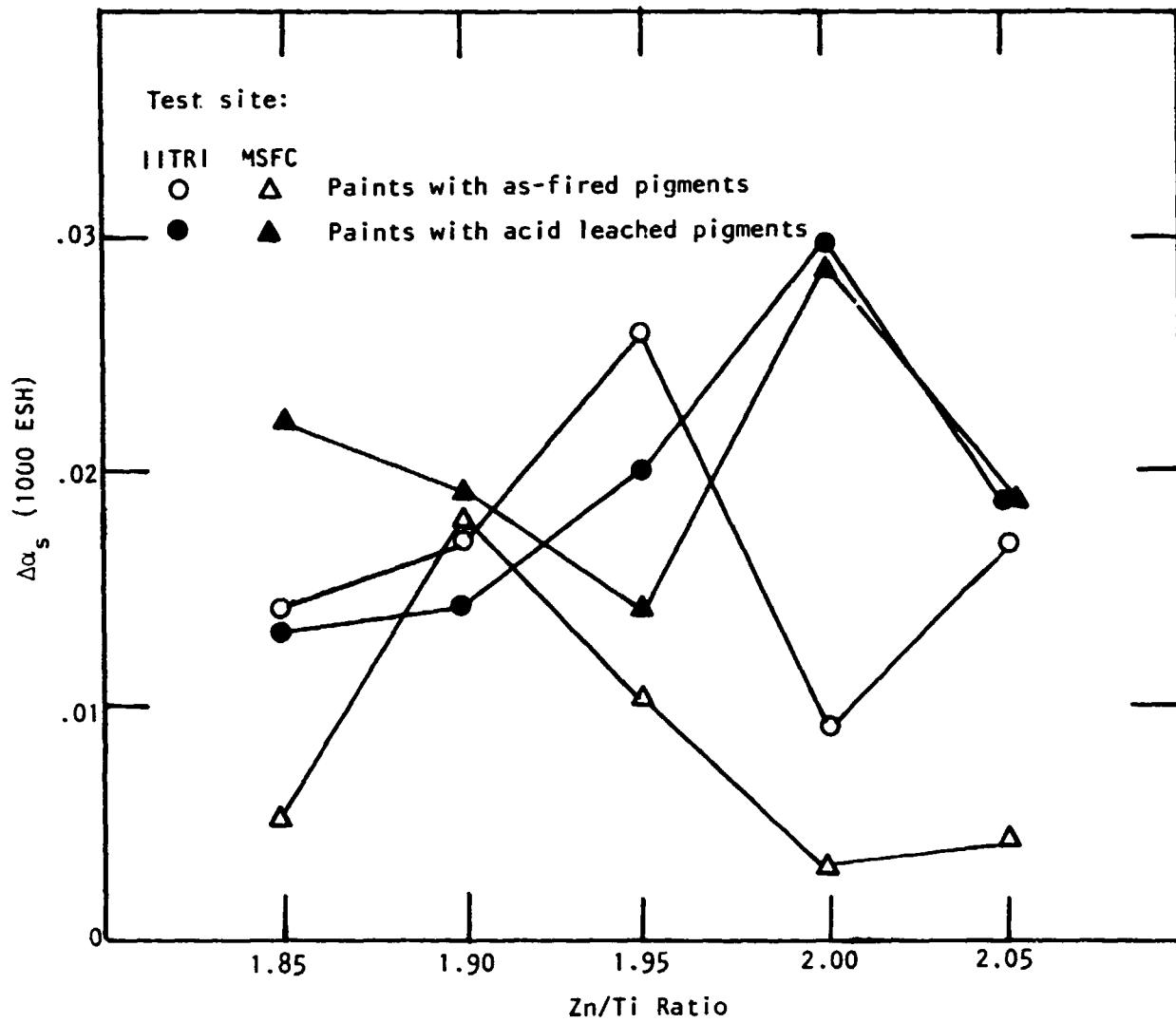
Figure 23. Solar absorptance changes (1000 ESH) for Zn_2TiO_4-silicate paints (900°C calcined pigments).
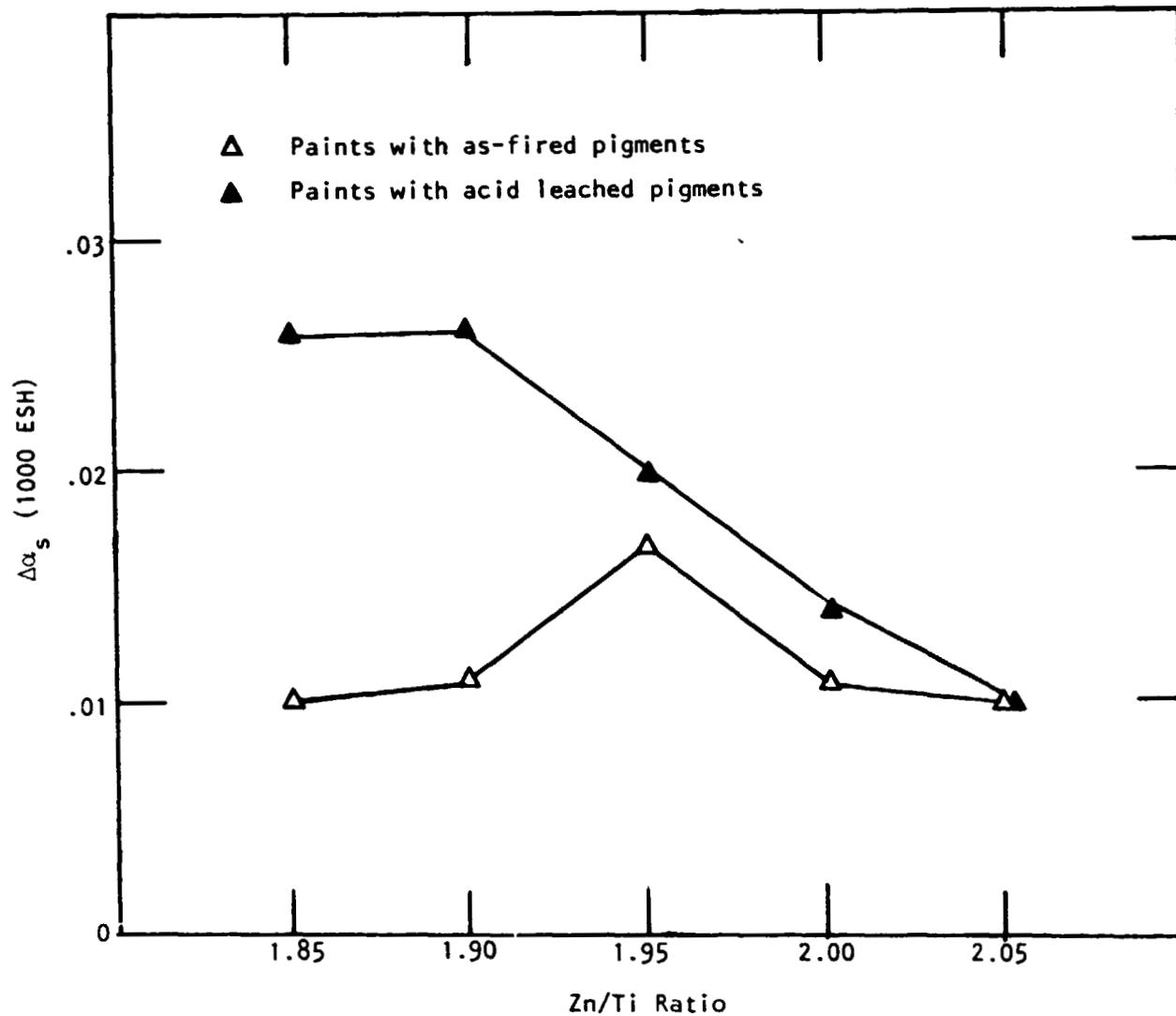
Figure 24. *Solar absorptance changes (1000 ESH) for Zn_2TiO_4-silicate paints (1050°C calcined pigments).*

TABLE 20.   REFLECTANCE CHANGES FOR SILICATE PAINTS
PIGMENTED WITH 1050°C Zn_2TiO_4 POWDERS (1000 ESH)

Sample	Change in Reflectance at Given Wavelength (microns)								
	.330	.354	.444	.554	.700	.929	1.30	1.71	2.50
5-10.5 Samples									
MOX-85(I)	1.0	0.5	0	0	1.0	1.5	0	+1.0	+1.0
(M)	0	0	1.5	1.5	2.0	2.0	0.5	+1.0	+1.5
MOX-90(I)	0	0	0	0.5	1.0	1.0	+0.5	+2.0	+3.0
(M)	0	0	1.0	1.0	2.0	2.5	1.0	+0.5	+1.0
MOX-95(I)	1.0	1.5	1.5	1.0	1.0	0.5	0.5	+1.5	+1.0
(M)	0	0	2.0	2.0	2.0	2.5	0.5	+2.0	+2.0
MOX-00(I)	1.0	0	1.5	1.0	1.0	2.0	0.5	+0.5	+2.0
(M)	0	0	0.5	1.5	1.5	2.0	0.5	+1.0	+1.5
MOX-05(I)	0	0	0	0.5	+0.5	1.0	0	+1.0	0
(M)	0	0.5	0.5	1.5	1.5	2.0	0.5	+1.0	+1.0
5-10.5-A-10 Samples									
MOX-85(I)	0	1.0	2.0	2.0	2.0	2.0	0	0	0
(M)	0	0	3.0	3.5	4.5	5.0	2.0	+1.5	+1.0
MOX-90(I)	1.0	3.0	1.5	1.0	1.0	1.0	0	0	+1.0
(M)	0	0	2.5	3.5	4.0	4.5	2.0	+1.0	+1.5
MOX-95(I)	1.0	2.0	2.0	1.5	1.5	2.0	0.5	0	+0.5
(M)	0	0	2.5	3.0	3.0	3.0	1.5	+0.5	+1.0
MOX-00(I)	0	2.0	1.0	1.0	0	0	0	+1.0	+2.0
(M)	0	0	2.0	2.0	2.0	2.5	1.0	0	+1.5
MOX-05(I)	0	0	0	0	0	1.0	0	0	0
(M)	0	0	1.5	1.0	2.0	2.0	0	+2.0	+2.0

Note: (I) = IITRI, (M) = MSFC.

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Figure 25. Additive reflectance changes vs. Zn/Ti ratio (1000 ESH)
for Zn_2TiO_4-silicate paints (1050°C calcined pigments).

TABLE 21.   STABILITY OF Zn_2TiO_4-SILICATE PAINTS

Sample No.	Zn/Ti Ratio	Calcination Temp., °C	PBR	$\alpha_{Initial}$	$\Delta\alpha_{1000}$ ESH
M2	1.95	900	4.26	.192	.006
M6	1.95	900	5.32	.169	.006
M10	1.95	900	7.09	.153	.004
M4	1.95	1050	4.26	.228	.004
M8	1.95	1050	5.32	.203	.003
M12	1.95	1050	7.09	.205	.005
M17	2.00	900	4.26	.190	.006
M14	2.00	900	5.32	.183	.003
M22	2.00	1050	4.26	.230	.008
M20	2.00	1050	4.26	.230	.008
M16	2.00	1050	5.32	.225	.004
M23	2.00	1050	7.09	.198	.006

These samples were generally more stable than those tested in the first 1000 ESH test (see preceding section). Higher pigment loadings were used in this test as compared to 1000 ESH (A) which could account for the improved stability. However four samples having a PBR of 4.3 were also included in 1000 ESH (B), and these were more stable than their 1000 ESH (A) counterparts. It is possible that improved quality control in the pigment processing may have eliminated some degradable contaminants in the Zn_2TiO_4 powder.

6.3.3 Test 5000 ESH

A long-term UV-vacuum exposure of 5000 ESH was conducted on a number of zinc orthotitanate coatings, described in Table -22. Some general observations may be made regarding water content in the paint formulations. Finer particle size pigments require higher water contents for proper fluidity in spraying, due to their higher surface area. As shown, "WC" varied from 46 to 91, reflecting differences in particle size. A second effect is that the lower WC compositions exhibited a more rapid thickness buildup during spraying. This behavior is reflected in the thicker coatings for 190(A) and 25. These different compositions represent a good cross-section of Zn_2TiO_4 development at IITRI.

The results of the 5000 ESH test are presented in Table 23 as changes in solar absorptance and emittance as a function of exposure. Reflectance spectra changes are shown in Figures 26 through 34. The data show that the zinc orthotitanate-potassium silicate paints (ZOT/PS7' were all fairly stable. Samples 3, 7, 14, 21, 29, and 44 exhibited changes in solar absorptance ranging from 0.011 to 0.026 which were lower than the 0.028 $\Delta\alpha_s$ shown by the Z93 sample (No. 25).

Somewhat anomalous behavior was shown by S13G/LO (sample 2, Figure 26). The increase of about 0.05 in α_s after 2500 ESH would be the expected degradation. However, the increase in reflectance (and decrease in α_s) after 5000 ESH is puzzling. Included in this test was a Zn_2TiO_4-pigmented RTV 602/LO coating (sample 19). This sample had a lower initial α_s as compared to S13G/LO, and displayed stronger degradation than the silicate-bonded samples.

The emittances for all samples were all fairly high. As has been the case in other space simulation tests, ϵ_T is essentially unaffected by UV-vacuum.

TABLE 22. ZINC ORTHOTITANATE PAINT SAMPLES
FOR 5000 ESH SPACE SIMULATION TEST

Sample No.	Zn/Ti Ratio	PBR	WC,[a] cc	Thickness, mils	Weight, g	Zn_2TiO_4 Code	Comments
2	(S13G/LO)	--	--	--	--	(ZnO)	Silicone-ZnO coating.
3	1.90	7.09	91	6.0	.2416	1112	Very fine particle size, made by mixed oxalate (MOX) method. TiOX of very small particle size used as precursor.
7	1.85	7.09	66	6.5	.2734	185	Standard, made by MOX method.
14	2.05	7.09	66	7.5	.2960	205	Standard, made by MOX method.
19	1.90	4.0	--	--	--	190(A)	RTV 602/LO binder.
21	1.90	7.09	46	10.0	.4178	190(A)	TiOX precursor prepared by direct $TiCl_4$ + oxalic acid reaction. For other Zn_2TiO_4 powders, a water solution of $TiCl_4$ is prepared, and this in turn is reacted with oxalic acid.
25	(Z93)	--	--	--	--	(ZnO)	Silicate-ZnO coating.
29	2.00	7.09	86	8.0	.3227	LH-112	Made by coprecipitation-calcination method. Appears to be of a particle size finer than standard MOX powders.
44	1.90	7.09	51	14.5	.6078	25	Standard, made by MOX method. Fairly coarse particle size.

[a]WC = Water content of paint formulation in cc H_2O per 100 g Zn_2TiO_4.

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TABLE 23. CHANGES IN SOLAR ABSORPTANCE AND EMITTANCE FOR
ZINC ORTHOTITANATE PAINTS AFTER 5000 ESH EXPOSURE

| Sample No.	$\Delta\alpha_s$ at Given ESH						ϵ_T	
	Initial	500	600	1000	2500	5000	Initial	5000 ESH
2	.184	.011	.040	.047	.051	.016	.901	.900
3	.149	.004	.007	.008	.013	.017	.907	.905
7	.131	.003	.007	.009	.014	.020	.885	.884
14	.155	.001	.002	.002	.007	.011	.893	.890
19	.170	.016	.016	.030	.037	.046	.857	.853
21	.174	.007	.006	.011	.013	.019	.896	.894
25	.174	.008	.004	.013	.021	.028	.896	.895
29	.122	.022	.004	.011	.016	.023	.890	.888
44	.157	.008	.008	.008	.014	.026	.885	.885
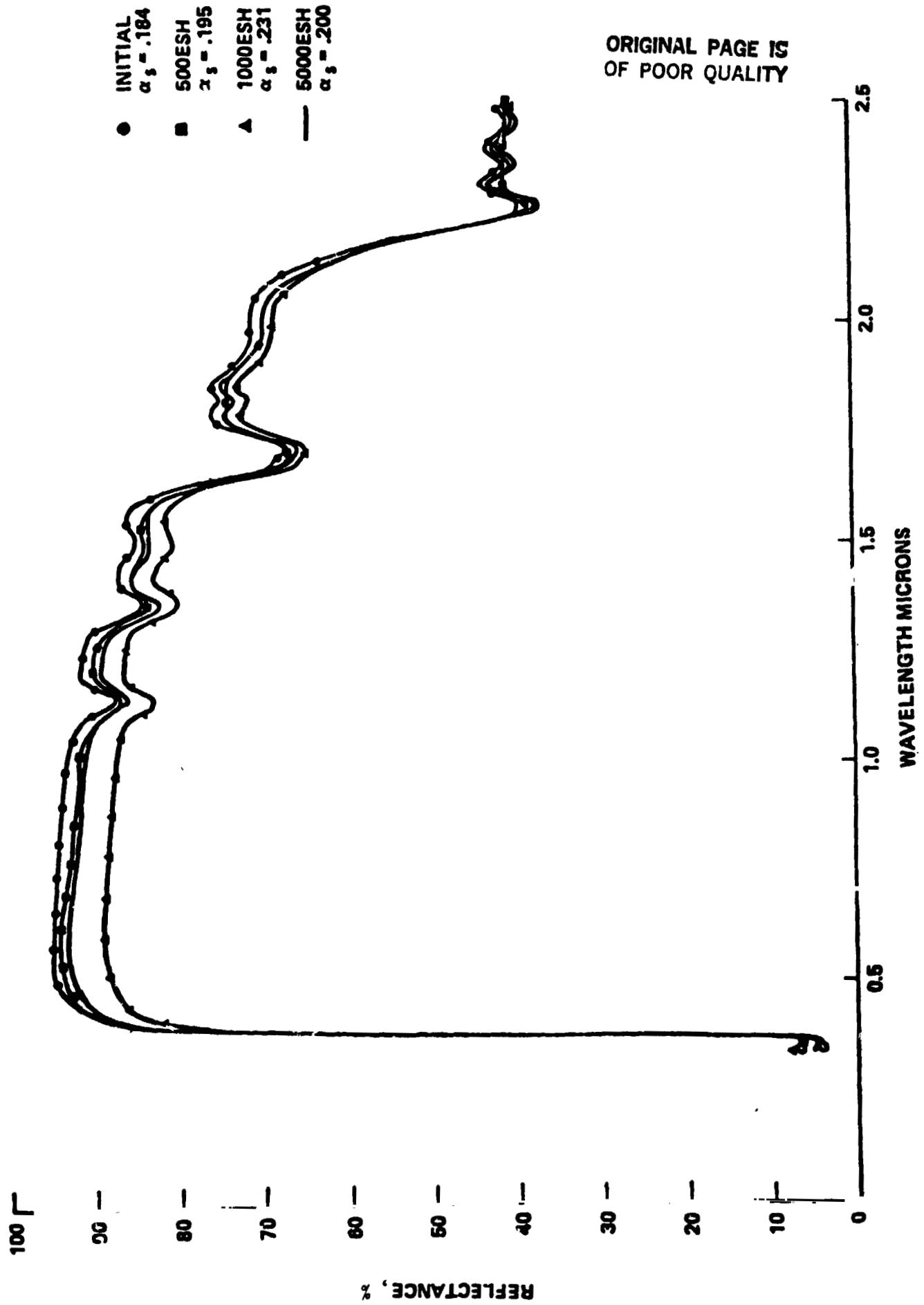
Figure 26. Reflectance changes for S13G/LO, sample 2 (5000 ESH).
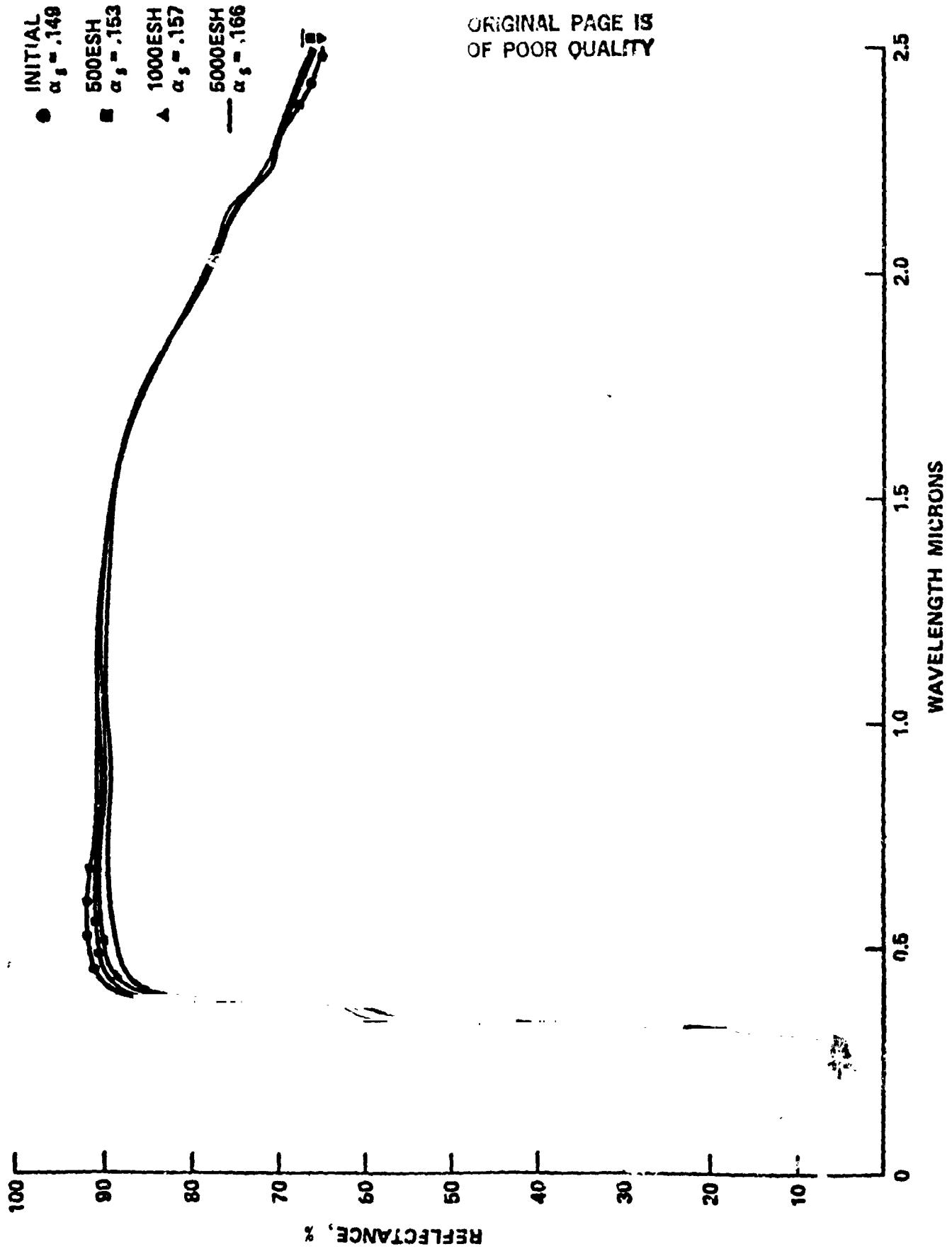
Figure 27. Reflectance changes for $Zn_2TiO_4/PS7$, sample 3 (5000 ESH).

INITIAL
$\alpha_s = .131$

COOESH
$\alpha_s = .134$

1000ESH
$\alpha_s = .140$

5000ESH
$\alpha_s = .151$

ORIGINAL PAGE IS
OF POOR QUALITY
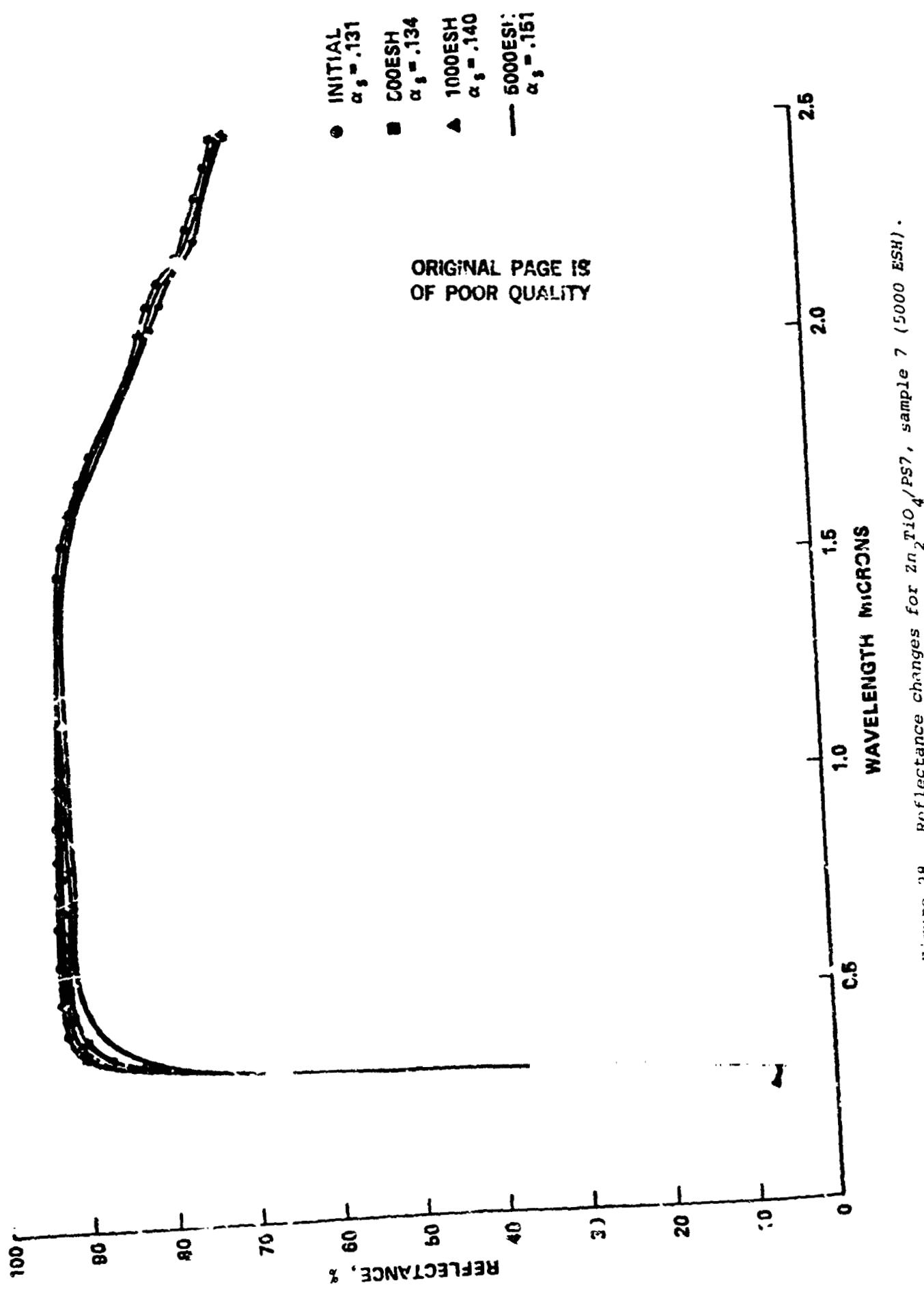
Figure 28. Reflectance changes for $Zn_2TiO_4/PS7$, sample 7 (5000 ESH).
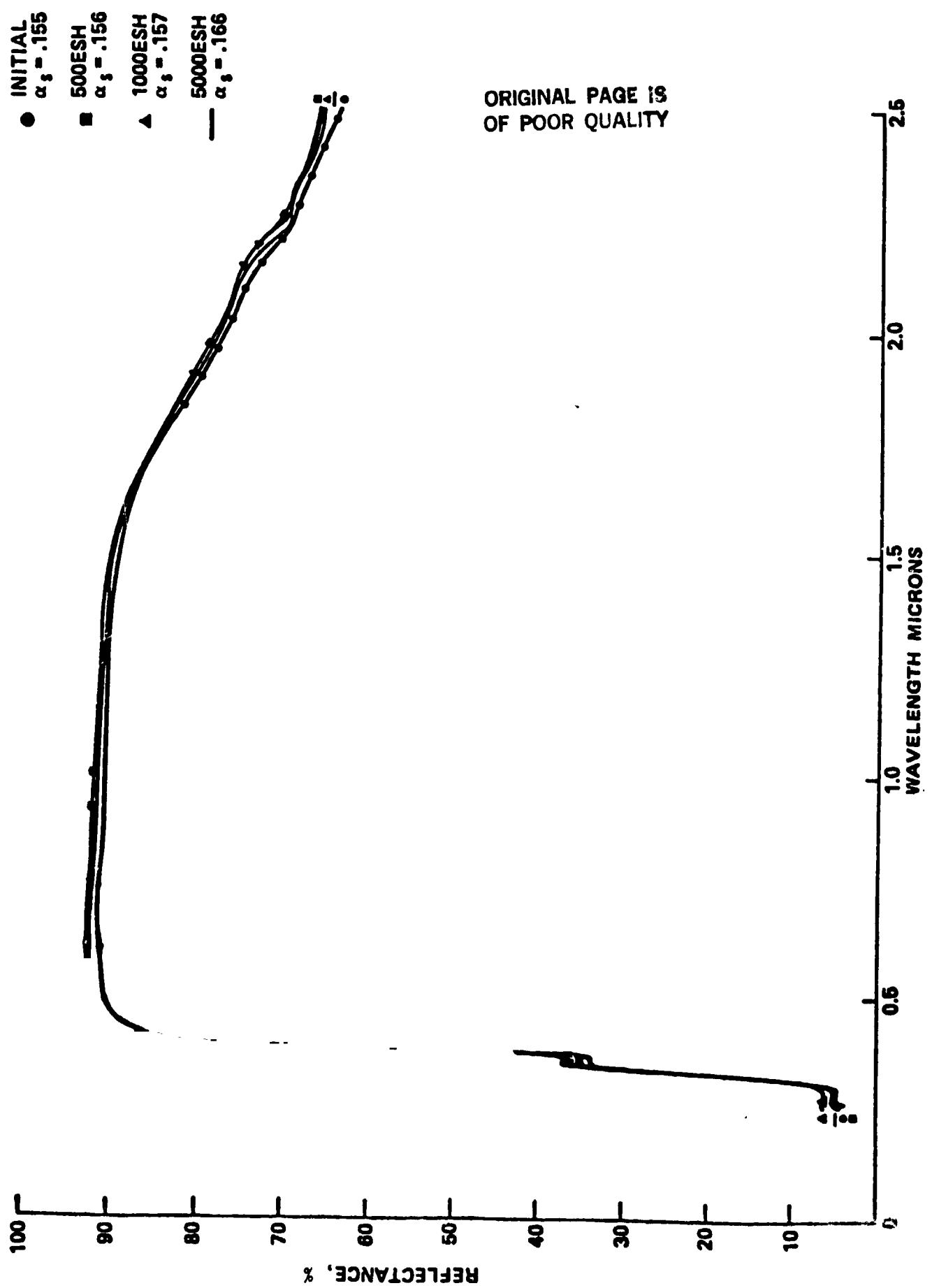
Figure 29. Reflectance changes for $Zn_2TiO_4/PS7$, sample 14 (5000 ESH).

INITIAL
● $\alpha_s = .155$

500ESH
■ $\alpha_s = .156$

1000ESH
▲ $\alpha_s = .157$

5000ESH
— $\alpha_s = .166$

WAVELENGTH MICRONS

REFLECTANCE, %

77
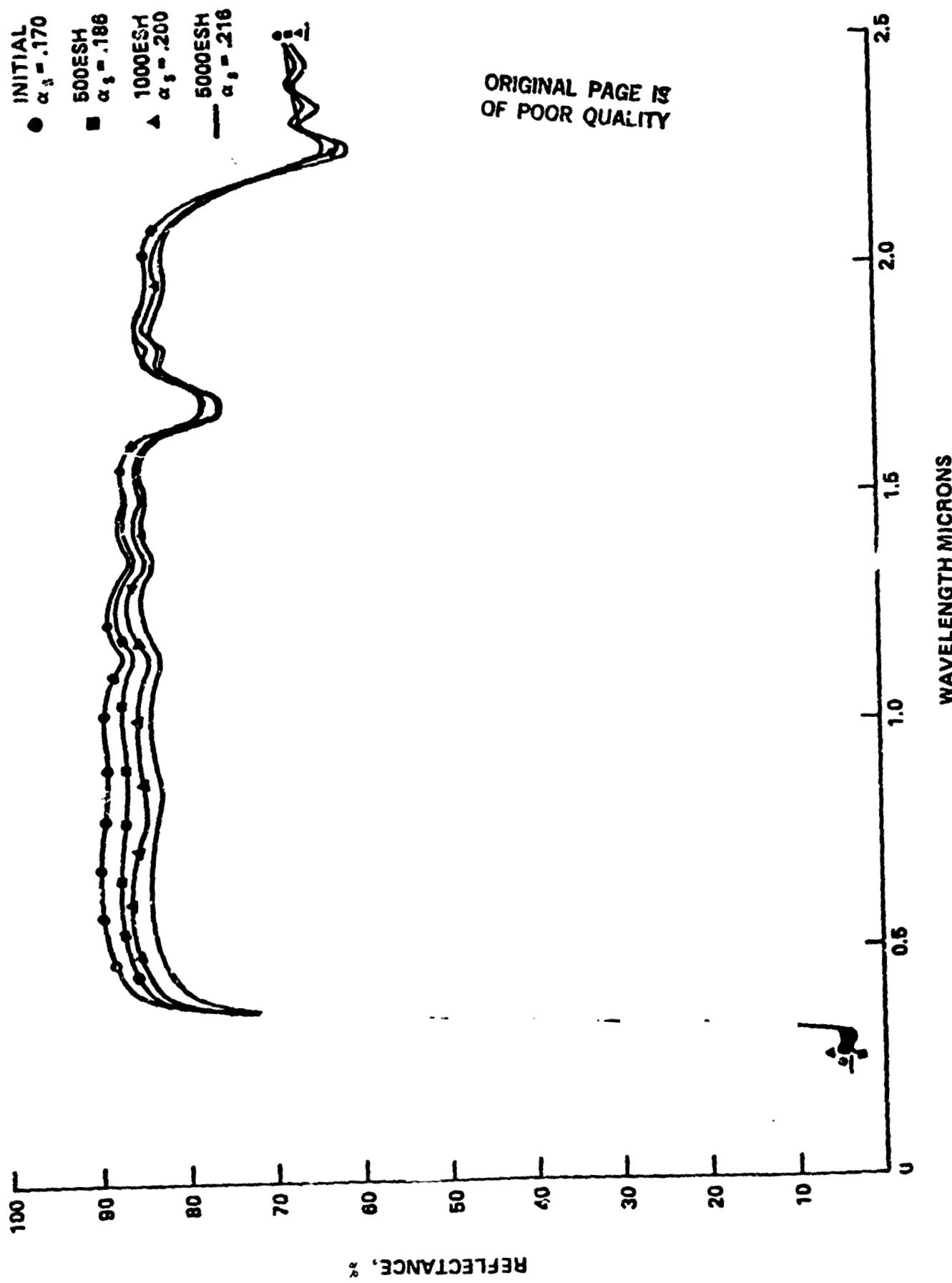
Figure 30. Reflectance changes for Zn_2TiO_4/RTV 602/LO, sample 19 (5000 ESH).

78
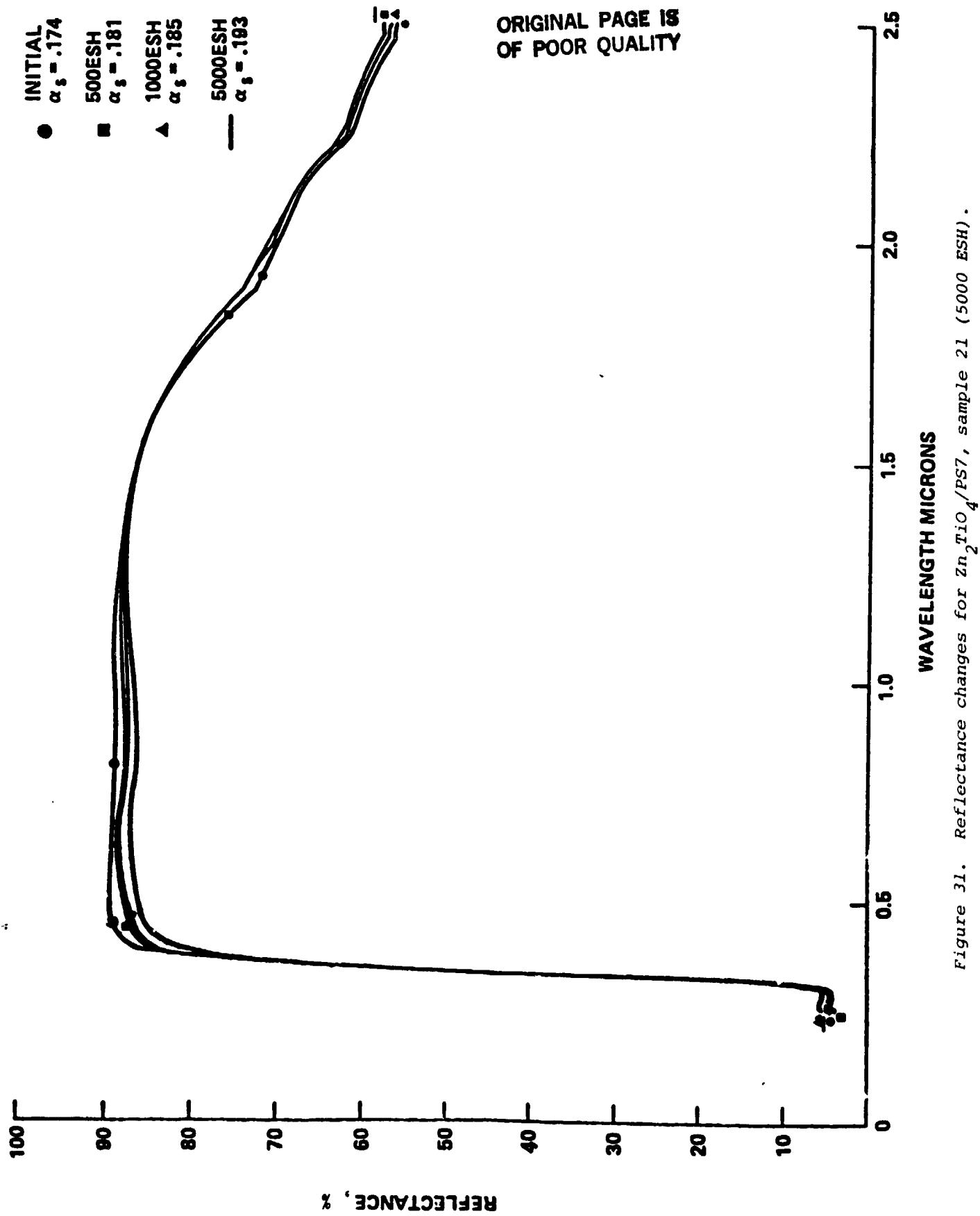
Figure 31. Reflectance changes for $Zn_2TiO_4/PS7$, sample 21 (5000 ESH).
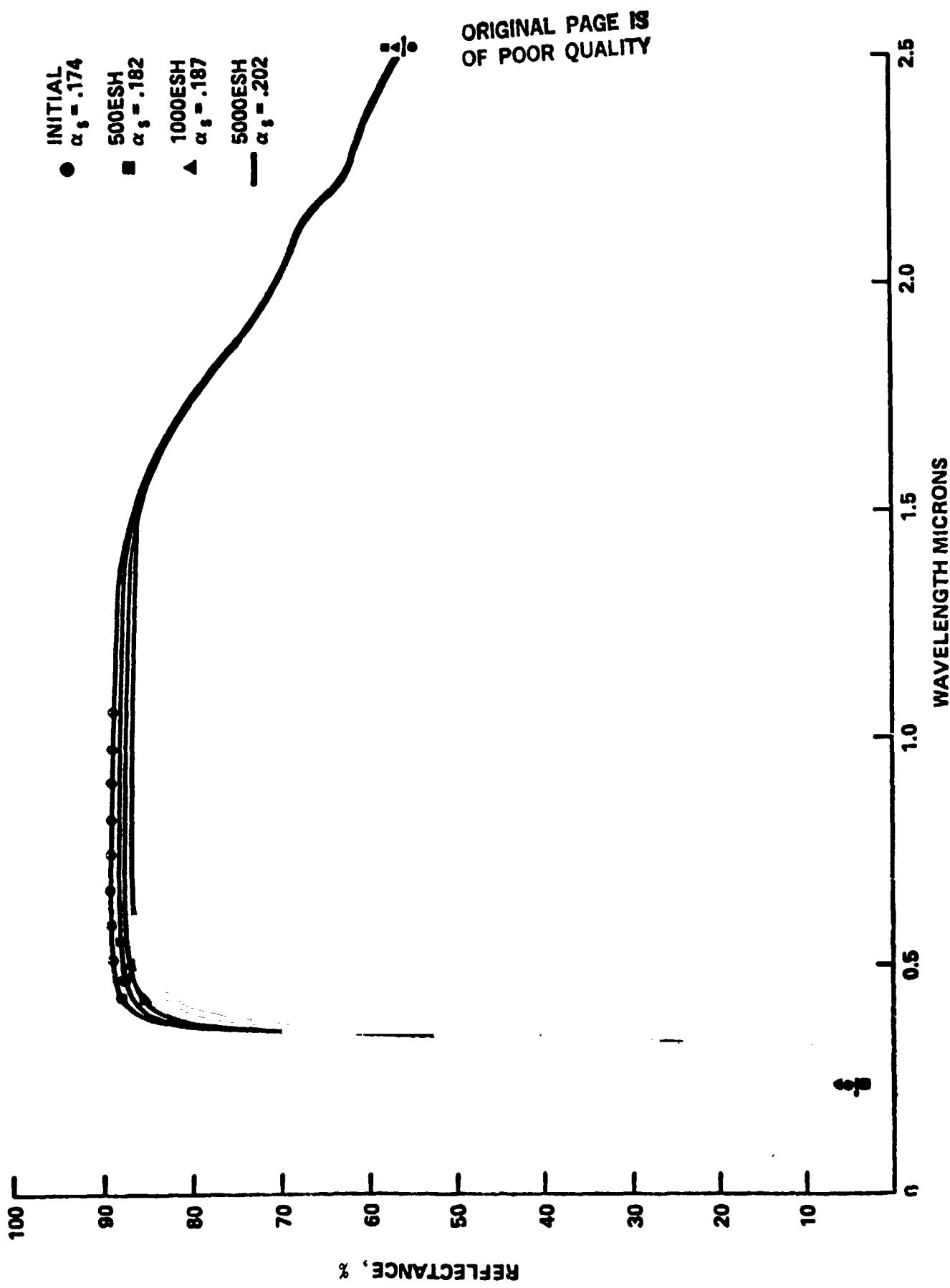
Figure 32. Reflectance changes for Z93, sample 25 (5000 ESH).

INITIAL
● $\alpha_s = .122$

500ESH
■ $\alpha_s = .124$

1000ESH
▲ $\alpha_s = .133$

5000ESH
— $\alpha_s = .145$

WAVELENGTH MICRONS
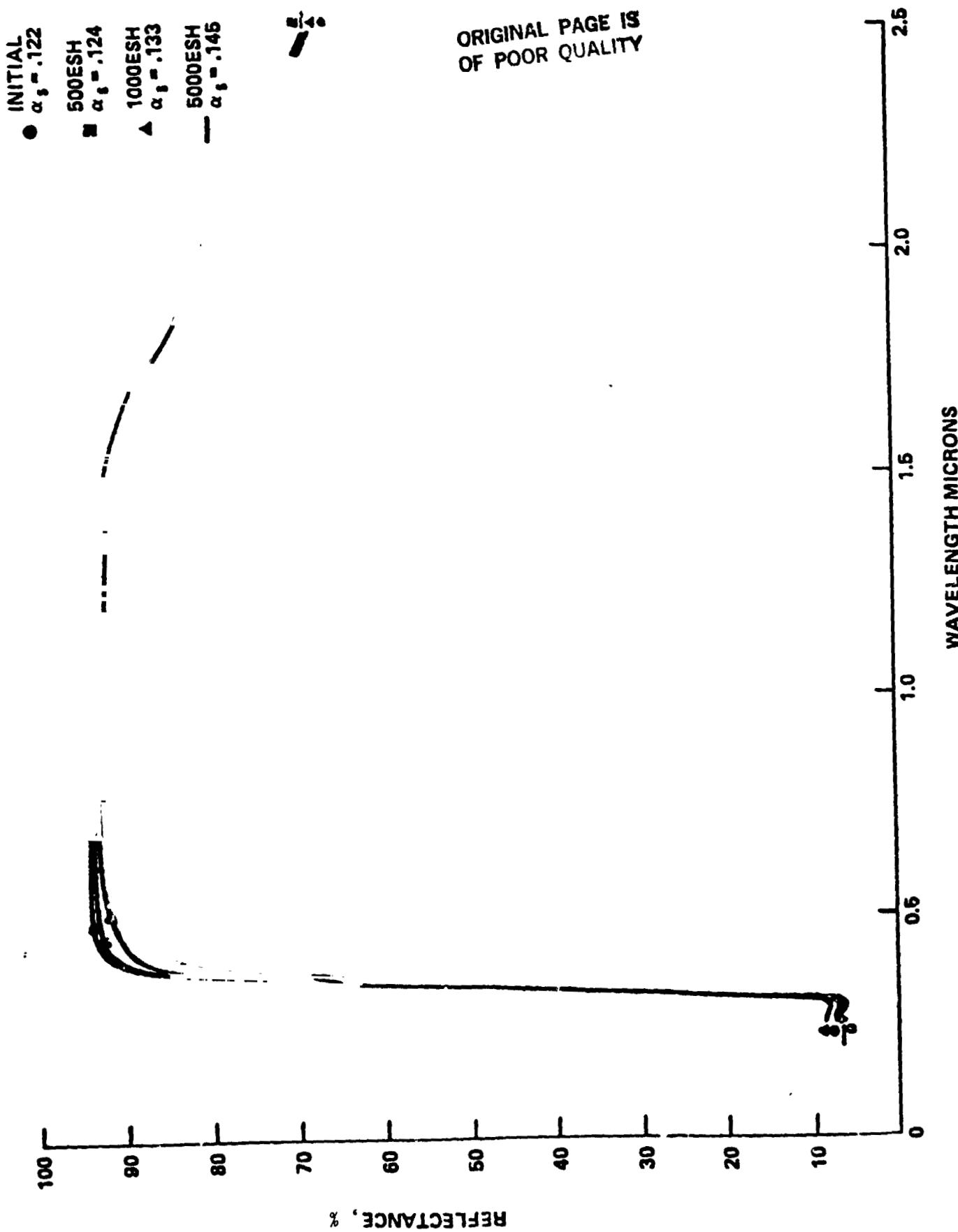
REFLECTANCE, %

Figure 33. Reflectance changes for $Zn_2TiO_4/PS7$, sample 29 (500 ESH).

81
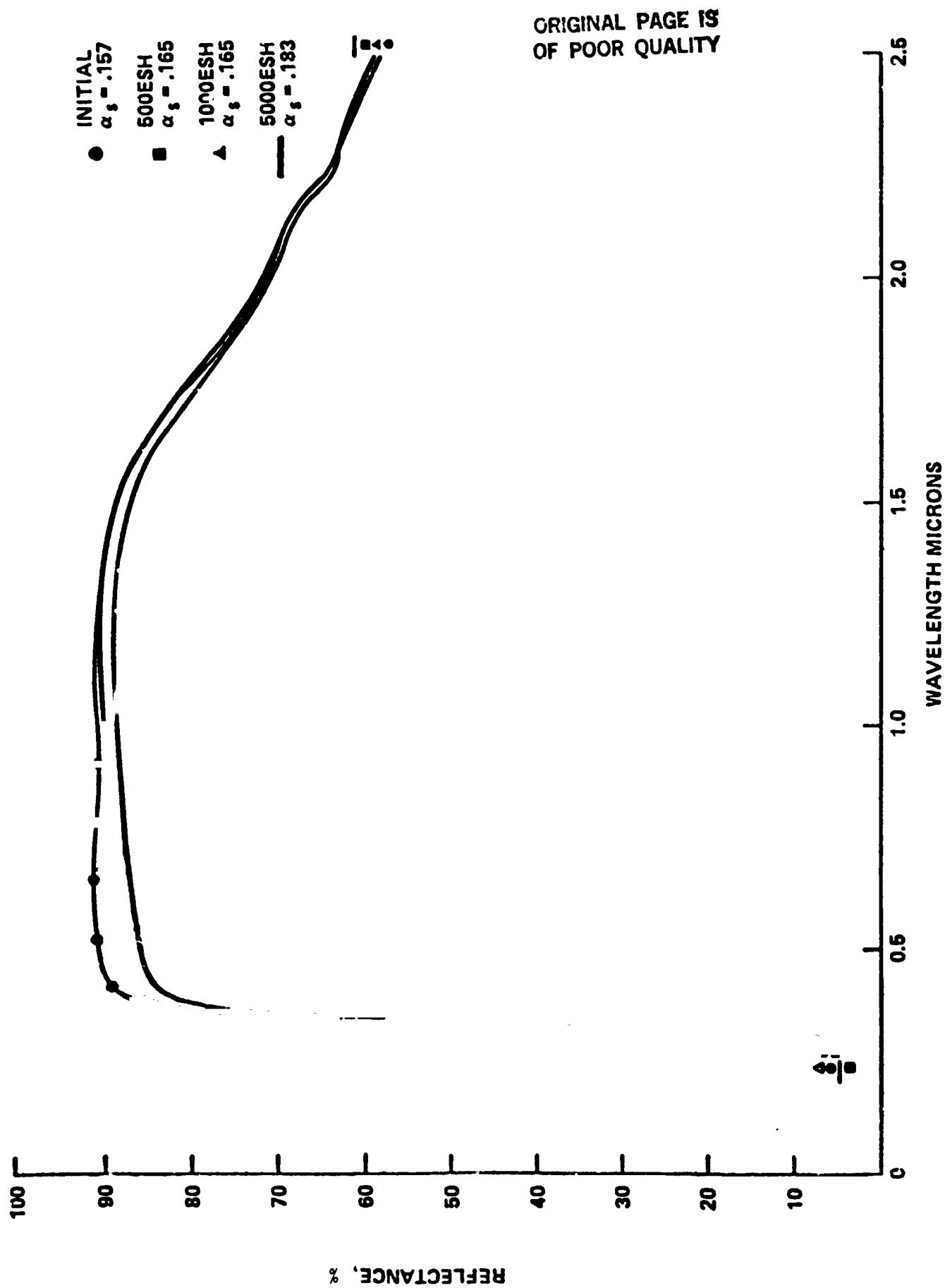
Figure 34. Reflectance changes for $Zn_2TiO_4/PS7$, sample 44 (5000 ESH).

6.4 SUMMARY

The space simulation studies conducted on this program have shown that zinc orthotitanate-potassium silicate coatings are as stable as Z93 in an ultraviolet-vacuum environment. Changes in α_S of about 0.2 after 5000 ESH can be expected. The Zn_2TiO_4 paints offer the advantage of a potentially lower initial α_S of about 0.11, which would yield a lower terminal α_S.

7. RECOMMENDATIONS FOR FUTURE WORK

The ultimate goal in the zinc orthotitanate paint system is to achieve a reproducible engineering material and full characterization of this material. It is recommended that the following studies be conducted to reach this goal.

7.1 PIGMENT PREPARATION STUDIES

7.1.1 Reproducibility in Powder Preparation

Studies should be conducted to achieve reproducibility in pigment powder preparation, i.e., synthesis of a particle size/shape to assure maximum reflectance or lowest solar absorptance. The studies will address variables in: (1) precursor chemical such as the chlorides and oxalic acid and their purity; (2) reaction/precipitation process; (3) filtration/drying procedure; (4) mixing technique of titanium and zinc oxalates; and (5) calcination techiques to obtain the final pigment powder. Microscopic and X-ray analysis will be used to monitor particle size and shape and chemical composition along the various steps of synthesis.

7.1.2 Coprecipitation (COP) vs. Mixed Oxalate (MOX) Method

The two synthesis methods should be examined for their respective ease of reproducibility of Zn_2TiO_4 and for amenability to scale-up. Although the MOX method produces a finer particle size powder than the COP method, the α_s of the respective paints are not greatly different (MOX = 0.11 vs. COP = 0.12). The COP method uses one less precipitation process and eliminates the need for ball milling to achieve powder mixing. Thus both processes should be compared in a single study.

7.2 PAINT STUDIES

7.2.1 Pigment to Binder Ratio (PBR)

PBR's for Zn_2TiO_4-PS7 paints have been varied from 4.3 to 10.6, with apparent good adhesion to aluminum substrates. These various compositions should be characterized as to physical properties (hardness, adhesion, cohesion density) and optical properties (reflectance vs. wavelength, reflectance

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vs. thickness). The guidance of actual users such as aerospace firms would be sought to determine optimum properties (or trade-off desired).

7.2.2 Spraying Characteristics

The effects of PBR and water content in the paint formulation on spraying should be examined. These include surface texture, water "flash" time, and predictability of thickness buildup.

7.2.3 Substrate Material

Historically, silicate-bonded paints such as Z93 have been found to adhere well to properly prepared metallic surfaces such as aluminum or magnesium. However, there appears to be a need to apply thermal control coatings onto polymeric substrates such as fiberglass, graphite composites or Kevlar. Studies will be performed to determine how to achieve optimum adhesion on such materials (e.g. substrate preparation and/or priming, spraying technique, cure method).

7.2.4 Space Qualification

Zinc orthotitanate-silicate paints need to be exposed to a simulated combined (ultraviolet plus high energy particulate radiation) environment test to determine their behavior in a synchronous orbit mission. Ultraviolet-vacuum test for 5000 ESH show Zn_2TiO_4 paints to be as stable as Z93 for near-earth orbits; the more stringent environment of a synchronous orbit needs to be addressed. The paint parameters to be examined in this test include:

- pigment-to-binder ratio
- stoichiometry i.e. Zn-to-Ti ratio
- substrate effects.

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